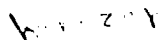


# ORGANIC CHEMISTRY OF BIVALENT SULFUR

VOLUME VI

by

  
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September 1965

E. EMMET REID

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## CHAPTER 1

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# Thiocyanic Acid and Derivatives

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The history of thiocyanates begins with an experiment by Porret in 1808. He heated Prussian blue with potassium sulfide and obtained a new salt from which several other salts were prepared.<sup>1427</sup> Then potassium ferrocyanide was fused with sulfur and more salts were studied. Several names were proposed for the new acid and many suppositions were made as to its composition. The fact that ammonia, a base, could be derived from an acid was especially puzzling.<sup>704, 1226</sup> Cyanogen and hydrogen sulfide were found to combine,<sup>627</sup> particularly when they were brought together in alcohol<sup>1901</sup> or in water.<sup>1124</sup> Treatment of the product with potassium hydroxide gave a solution in which potassium thiocyanate, sulfide, and cyanide were identified.<sup>1124</sup>

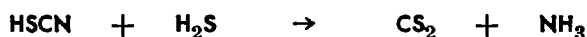
Zeise approached modern practice by preparing ammonium thiocyanate from ammonia and carbon disulfide.<sup>1431</sup> The relation of this to thiourea was recognized later.<sup>1485</sup> The name "thioprusic acid" was suggested by Claus.<sup>352b</sup>

### Thiocyanic Acid—HSCN

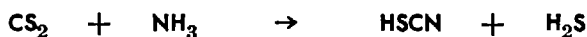
Although salts of thiocyanic acid are readily available, the free acid is difficult to isolate in a pure condition and still harder to keep. This problem has engaged the attention of chemists for more than a century.

In 1821, Wöhler treated mercury thiocyanate with hydrogen

sulfide and obtained a distillate that was unstable.<sup>1901</sup> Distillation of metal thiocyanates with dilute aqueous acids gave carbon dioxide and disulfide, hydrogen sulfide, and ammonia. Only under special conditions can thiocyanic acid be distilled.<sup>1931</sup> Thiocyanates of heavy metals are acted on incompletely by hydrogen sulfide, but the free acid has been obtained as an ether-like liquid by passing dry hydrogen sulfide over mercuric thiocyanate. The thiocyanic acid may be destroyed by the hydrogen sulfide: 1842, 1830a, 1830d, 1830e



Ammonia and carbon disulfide passed through a glowing hot porcelain tube and into water have been said to give thiocyanic acid: 1573b



An aqueous solution of it can be obtained by distilling potassium thiocyanate and dilute sulfuric acid,<sup>786</sup> or from the silver<sup>1019</sup> or lead salt suspended in water and hydrogen sulfide.<sup>1947</sup> A 20% aqueous solution can be prepared quickly and in almost quantitative yield by dropping equivalent aqueous solutions of ammonium thiocyanate and sulfuric acid into a flask kept at 60° under reduced pressure.<sup>663a</sup> A 15% solution is stable if kept cold.

A 20% solution of thiocyanic acid in *i*-amyl alcohol was obtained from the extraction of an aqueous solution of ammonium thiocyanate acidified with sulfuric acid.<sup>1717</sup> Powdered sodium thiocyanate may be covered with a solvent such as carbon tetrachloride and 50% aqueous sulfuric acid added with vigorous stirring. The nonaqueous layer is separated and dried over phosphoric anhydride.<sup>970a</sup> To a saturated aqueous solution of ammonium thiocyanate, 50% sulfuric acid is added at -5° and the mixture is extracted with enough ether to obtain not over a 20% solution, which is dried.<sup>108</sup>

Thiocyanic acid in concentrated solution in ether at 0°, gradually decomposes with the formation of perthiocyanic acid, hydrocyanic acid, and hydrogen sulfide. This reaction has been studied kinetically.<sup>165</sup> Thiocyanic acid and ammonium thiocyanate can be volatilized without decomposition by spraying their aqueous solutions into a heated flask in a current of hot air or steam.<sup>663c</sup>

When cold hydrochloric acid is added to cold potassium thio-

cyanate solution at 40 mm pressure, thiocyanic acid passes over and is condensed as a straw-colored, polymeric solid in a freezing mixture.<sup>1207</sup> It is similarly obtained from a mixture of potassium thiocyanate, phosphorous pentoxide, and concentrated sulfuric acid.<sup>1521</sup> The monomeric acid has been prepared by grinding potassium bisulfate and potassium thiocyanate<sup>1532</sup> together in a high vacuum, passing the gas over phosphoric anhydride, and condensing it at  $-190^{\circ}$  as a white solid which melts at  $-110^{\circ}$  C. When warmed to  $-90^{\circ}$  this polymerizes to a white mass which does not melt.<sup>164, 166</sup>

A solution of thiocyanic acid has been prepared by passing an aqueous solution of an alkali salt through a column containing the resin-exchanger Wofatit KS.<sup>1021</sup>

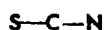
### STRUCTURE

Different conclusions have been reached as to the structure of thiocyanic acid. The Raman spectrum indicates that the thiocyanate ion is  $\text{N}:\text{C}:\text{S}-$ ,<sup>1082</sup> whereas the mean refraction value for the  $-\text{SCN}$  group is 23.3 in organic compounds, and in inorganic, 28.1.<sup>441b, 441c</sup> The molecular magnetic rotations for several wave lengths have been measured. A comparison of these data for ethyl isothiocyanate indicates that the acid is  $\text{HNCS}$ .<sup>619</sup> A comparison of the ultraviolet absorption spectra of mercuric thiocyanate with ethyl thiocyanate and isothiocyanate indicates the structure  $\text{Hg}(\text{NCS})_2$ .<sup>616</sup> The Raman spectra of methyl and ethyl thiocyanates and isothiocyanates, and of thiocyanic acid, pure and in solution, suggests that there is no mesomerism of the  $\text{SCN}$  group.<sup>687</sup> The observed frequencies in the Raman and in the infrared spectra of some thiocyanates of silicon point to an isothiocyanate structure and appreciable double-bond character.<sup>688</sup> A considerable amount of double-bond character in the  $\text{C}-\text{S}$  bond of thiocyanates has been reported.<sup>928</sup>

The apparent volume<sup>518</sup> and the diamagnetic susceptibility<sup>1792</sup> of the thiocyanate ion have been measured. The heat of formation of thiocyanic acid in solution is 19.9 Cal.<sup>908</sup> A dissertation has been written on the thermodynamic properties of isothiocyanic acid.<sup>221</sup>

The molecule of thiocyanic acid is made up of four atoms, each of a different element, each having a different valence. It con-

tains in its simplest form a single carbon atom combined with sulfur and nitrogen.



This grouping is the core of a large proportion of important organic compounds of sulfur. It is present in cysteine,  $\text{HS}\cdot\text{C}(\text{NH}_2)\text{COOH}$ ; in thioamides,  $\text{RCS}\cdot\text{NH}_2$ ; in thiocarbamates,  $\text{H}_2\text{N}\cdot\text{CS}\cdot\text{SH}$ ,  $\text{RNH}\cdot\text{CS}\cdot\text{SH}$ ; and in thiourea, which with its derivatives, fills almost half of Volume V of this series and part of this volume.

Most of these compounds can be considered as formed by the addition of water, ethanol, ammonia, amines, hydrogen sulfide, or mercaptans to one or the other form of thiocyanic acid; see Table 1.1. This does not mean that they are produced simply by pouring thiocyanic acid into one of these compounds. The additions are made with paper and pencil because such additions require no catalyst. The free acids are written though some of them exist only as salts or esters. Except when the hydrogen atoms are substituted by alkyls, isomerism exists among the addition products as it does between the two forms of thiocyanic acid.

TABLE 1.1  
*Addition Products of Thiocyanic Acids*

<i>From addition of</i>	<i>Thiocyanic Acid</i>	<i>Isothiocyanic Acid</i>
	HSCN	SCNH
Water	$\text{HS}\cdot\text{CO}\cdot\text{NH}_2$	$\text{HO}\cdot\text{CS}\cdot\text{NH}_2$
Hydrogen sulfide	$(\text{HS})_2\text{C}:\text{NH}$	$\text{HS}\cdot\text{CS}\cdot\text{NH}_2$
ROH	$\text{ROC}(:\text{NH})\text{SH}$	$\text{RO}\cdot\text{CS}\cdot\text{NH}_2$
RSH	$\text{RSC}(:\text{NH})\text{SH}$	$\text{RS}\cdot\text{CS}\cdot\text{NH}_2$
Ammonia	$\text{HS}\cdot\text{C}(:\text{NH})\text{NH}_2$	$\text{H}_2\text{N}\cdot\text{CS}\cdot\text{NH}_2$
$\text{RNH}_2$	$\text{HS}\cdot\text{C}(:\text{NH})\text{NHR}$	$\text{RHN}\cdot\text{CS}\cdot\text{NH}_2$
$\text{R}_2\text{NH}$	$\text{HS}\cdot\text{C}(:\text{NH})\text{NR}_2$	$\text{R}_2\text{N}\cdot\text{CS}\cdot\text{NH}_2$

It is interesting to compare isothiocyanic acid with carbon disulfide and carbodiimide, in which the oxygen of carbon dioxide may be considered as substituted by sulfur atoms or imido groups. Isothiocyanic acid is a cross between these, one oxygen being substituted by sulfur and the other by the imido group; see Table 1.2.

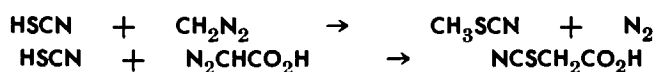
TABLE 1.2  
Reaction Products of Isothiocyanic Acid and  
Analogous Compounds

From addition of	Carbon Disulfide	Isothiocyanic Acid	Carbon Dithide
	S:C:S	S:C:NH	HN:C:NH
Water	HS·CO·SH	HS·CO·NH <sub>2</sub>	H <sub>2</sub> N·CO·NH <sub>2</sub>
ROH	RO·CS·SH	RO·CS·NH <sub>2</sub>	RO·CO·NH <sub>2</sub>
Hydrogen sulfide	HS·CS·SH	HS·CS·NH <sub>2</sub>	HS·C(:NH)NH <sub>2</sub>
RSH	RS·CS·SH	RS·CS·NH <sub>2</sub>	RS·C(:NH)NH <sub>2</sub>
Ammonia	HS·CS·NH <sub>2</sub>	HS·C(:NH)NH <sub>2</sub>	H <sub>2</sub> N·C(:NH)NH <sub>2</sub>
An amine	HS·CS·NHR	HS·C(:NH)NHR	H <sub>2</sub> N·C(:NH)NHR

#### REACTIONS OF THIOCYANIC ACID

When an aqueous solution of potassium thiocyanate is acidified and extracted with ether, an addition compound,  $\text{HSCN} \cdot \text{Et}_2\text{O}$ , is formed.<sup>1019</sup> With alcohols,  $\text{HSCN} \cdot 2 \text{ MeOH}$  and  $\text{HSCN} \cdot 2 \text{ EtOH}$  have been isolated.<sup>108, 1019</sup> Triphenylmethyl thiocyanate is obtained by the reaction of triphenylmethyl chloride with free thiocyanic acid in the presence of sulfuric acid.<sup>157, 1126</sup> The reaction appears to be ionic and is similar to that with triphenylcarbinol.<sup>1481b</sup>

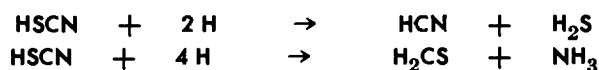
Thiocyanic acid is esterified by diazomethane<sup>1363</sup> or by diazoacetic acid:<sup>828a</sup>



The products are thiocyanates rather than mustard oils. Some ethyl thiocyanate is obtained when potassium thiocyanate and sulfuric acid are brought together in alcohol solution. A by-product is perthiocyanic acid.<sup>786</sup> When sulfuric acid is added to an acetic acid solution of triphenylcarbinol and ammonium thiocyanate, triphenylmethyl thiocyanate is precipitated in high yield.<sup>1481b</sup>

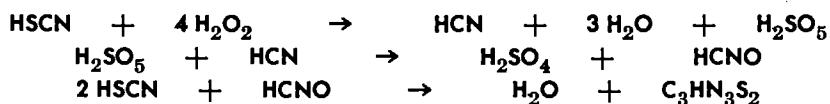
Thiocyanic acid vapor is decomposed by an electric discharge into hydrocyanic acid and sulfur.<sup>629, 661</sup>

Thiocyanic acid is reduced by nascent hydrogen:<sup>813, 814</sup>

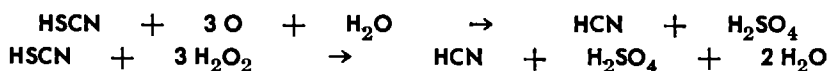


The second reaction has been questioned.<sup>1642</sup> The hydrocyanic acid may go to methylamine.<sup>813, 814, 1642</sup>

According to the reagents and the conditions, the oxidation of thiocyanic acid and its salts may lead to quite different products. Oxidation by nitric acid<sup>368, 1812</sup> or by electrolysis<sup>428</sup> removes the sulfur, leaving hydrocyanic acid. A 30% solution of hydrogen peroxide reacts explosively with a concentrated thiocyanate solution.<sup>1345b</sup> Under other conditions Caro's acid may be an intermediate product:<sup>1752a</sup>



The reaction between peroxy compounds and thiocyanate ions has indicated that Caro's acid is not due to formation of solvate peroxy acids but is the result of an induction reaction.<sup>389</sup>  $\text{OsO}_4$  is a catalyst in the oxidation of the thiocyanate ion by the ferricyanide ion.<sup>1689</sup> Lead and lead oxide remove the sulfur from quinidine thiocyanate, leaving the cyanide.<sup>284</sup> Thiocyanic acid is oxidised more rapidly than its salts:<sup>954</sup>

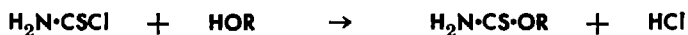


Thiocyanogen has been found to be an intermediate product in the chromate oxidation.<sup>1839</sup> In the oxidation of ammonium thiocyanate by nitric acid, about 10% of the nitrogen is lost on account of the formation of ammonium nitrite.<sup>662</sup> The oxidation of thiocyanic acid vapor in air depends on the nature of the contact surfaces. Hydrocyanic acid and sulfur dioxide may be produced.<sup>663c</sup> The thiocyanate ion may be oxidised electrolytically.<sup>626</sup> Equations have been set up relating the oxidation-reduction potentials of systems that involve thiocyanate ions.<sup>626</sup> A potentiometric study involving the mechanism of reduction of the thiocyanate ion in both acid and alkaline medium has been made.<sup>626</sup> The reducing power of mercury in the presence of thiocyanate ion is greatly enhanced.<sup>274, 275</sup> The electrolysis of thiocyanates gives, in decreasing order of yield, sulfates, hydrocyanic acid, perthiocyanogen, and ammonia.<sup>1502</sup>

Dry hydrogen chloride adds to thiocyanic acid in dry ether:<sup>108, 1019</sup>



The compound decomposes at 75–80° without melting and reacts as an acid chloride with an alcohol giving a xanthogen amide:



In the case of methanol there is some of the isomeric thiol ester,  $\text{H}_2\text{N}\cdot\text{CO}\cdot\text{SMe}$ .<sup>108, 109, 178, 1472a</sup> In ether, thiocyanic and cyanic acids combine:



With ethanol, this forms a monothioallophanic ester which melts at 180°:<sup>170</sup>

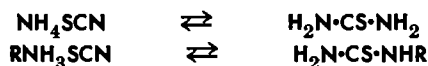


When sulfuric acid is added to a mixture of ammonium thiocyanate and an alcohol, a mono-thiocarbamate is formed:



The thion-ester, which is the primary product, isomerizes into the thiol-ester.<sup>109, 178</sup>

An important reaction of HSCN is the isomerizing of its ammonium—or substituted ammonium—salts to thiourea<sup>1834</sup> or substituted thioureas:



This may be regarded as addition of ammonia to isothiocyanic acid:



At higher temperatures the equilibrium is shifted to the right. It is further to the right for substituted ammonium thiocyanates. The reaction goes far toward completion when the substituted thiourea is only sparingly soluble and separates out. Thus, phenyl thiourea is prepared by refluxing a solution of ammonium thiocyanate and aniline hydrochloride. The isomerizing of phenyl-<sup>715</sup> methyl-<sup>714</sup> and benzyl-<sup>714</sup> ammonium thiocyanates has been particularly investigated. This isomerization has been considered extensively in Volume V, where several additional examples are given. From peri-diaminonaphthylene and thiocyanic

acid, a cyclic thiourea,  $C_{10}H_8(NH)_2CS$ , is formed.<sup>1545</sup> From potassium thiocyanate and 2,4-dibromo-5-aminomethylglyoxaline the corresponding thiourea has been obtained.<sup>1250</sup> A disinfectant is said to be prepared similarly.<sup>1859</sup>

When other reactive groups are properly placed, the addition products first formed rearrange or condense to form cyclic compounds.  $\beta$ -Aminolevulinic acid and potassium thiocyanate give 2-thiol-4-methylimidazolyl-5-acetic acid, m.  $276^\circ$ .<sup>1747</sup> For the synthesis of histamine,  $\alpha,\gamma$ -diaminobutyric acid was the starting point, and the 2-mercapto derivative of histamine was an intermediate product.<sup>13</sup>

When  $\beta$ -bromomethylamine hydrobromide and potassium thiocyanate are brought together, the thiocyanic acid that is liberated combines with the amine to form  $\beta$ -bromomethylthiourea:



This is an alkyl halide at one end and a thiourea at the other. Hence, it forms cyclic ethylene-pseudothiourea hydrobromide which turns out to be an aminothiazoline salt: 606b, 606a, 806, 1190, 1203



The  $\gamma$ -bromopropylamine is the starting point for a similar series of reactions leading to the trimethylene compound.<sup>610</sup> From bis ( $\beta$ -chloroethyl)-amine hydrochloride, 2-imino-3-( $\beta$ -chloroethyl) thiazolidine is derived.<sup>1436</sup> Similar reactions take place starting with  $\beta$ -phenyl- $\beta$ -chloroethyl amine hydrochloride<sup>1905</sup> and  $\beta$ -bromo- $\alpha$ -methylethyl amine hydrobromide.<sup>611</sup> In much the same way sodium thiocyanate and the dihydrochloride of  $\alpha,\delta$ -diamino- $\gamma$ -ketovaleric acid have been used in the synthesis of 2-thiolhistidine.<sup>55</sup>

Thiolglucimidazole has been obtained by condensing glucosamine with thiocyanic acid.<sup>880, 1383</sup>  $\mu$ -Thiolglucosaxoline and  $\mu$ -thiolfructosaxoline have been prepared, starting with glucose<sup>943, 1934</sup> and fructose<sup>943, 1933</sup> and adding thiocyanic acid.

At  $140^\circ$  the thiocyanate of trimethylene diamine is converted to trimethylene thiourea.<sup>1101</sup>

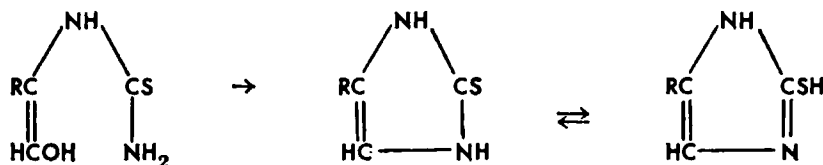
The addition of thiocyanic acid to thioglycolic acid gives a dithiourethane:





which loses water to form the cyclic rhodanic acid.<sup>35a</sup> Thiocyanic acid and dicyandiamid give a 47% yield of thioammeline, which forms salts with bases.<sup>1472b</sup>

The thiourea from an amino-aldehyde thiocyanate loses a molecule of water:



The aldehyde is written in the *enol* form. The product is a 2-mercapto-5-alkyl-imidazole.<sup>12, 1189, 1330b</sup> An amino-ketone, of the type  $\text{NH}_2\text{CH}_2\text{COR}$ , gives a 2-mercapto-4-alkyl imidazole.<sup>612, 1037</sup> If the  $-\text{NH}_2$  is in any other alkyl there will be alkyl substituents in both the 4 and the 5 positions.<sup>128, 277, 527, 613, 885, 896, 1062, 1330a</sup> A second amino group remains as such in a side chain.<sup>1034, 1455</sup>

The condensation of methyl ethyl ketone with a mixture of hydrocyanic and thiocyanic acids gives 5-methyl-5-ethyl-2-thio-4-oxo-oxazolidene.<sup>504</sup>

Glycine and potassium thiocyanate give the free thiohydantoic acid which, when heated with hydrochloric acid, condenses to 2-thiohydantoin.<sup>750, 912a, 1014, 1038</sup> This is the basic reaction for the preparation of thiohydantoins which have been considered in Volume V, Chapter 5. Tolythiohydantoin is obtained from glycine and *p*-thiocyananiline.<sup>1451</sup> Pyrrolidene-carboxylic acid and potassium thiocyanate in acetanhydride give the thiohydantoin of pyrrolidone carboxylic acid, which is hydrolyzed to 2-thiohydantoin-4-propionic acid. The carboxyl terminal of a polypeptide is determined by treating it with  $\text{NH}_4\text{SCN}$  and acetanhydride and hydrolyzing to the thiohydantoin.<sup>764</sup>

The thiocyanate of  $\text{Ph}(\text{Cl})\text{CH}-\text{CH}_2\text{NH}_2$  yields 2-amino-thiazoline;<sup>607c</sup> and that of  $\text{Ph}-\text{CH}(\text{NH}_2)\text{CH}(\text{CH}_3)\text{COOH}$  yields 4-phenyl-5-methyldihydrothiouracil.<sup>1428</sup> 2-Phenyl-semicarbazide thiocyanate is prepared from thiocyanic acid and 2-phenyl semicarbazide.<sup>1385</sup>

The dry distillation of potassium thiocyanate gives a compound known as mellone.<sup>1123d</sup> From ammonium thiocyanate at high temperatures—200 to 400°—a variety of decomposition and

condensation products are obtained, some of which are related to thiourea. Some that have been identified are a perthio acid, thiobiuret, carbon disulfide, guanidine and its thiocyanate, melam and melamine.<sup>352a, 353, 354, 416, 1830b</sup> Melamine is obtained by heating ammonium thiocyanate or a mixture of potassium thiocyanate and ammonium chloride.<sup>352c, 1104, 1123b, 1123e, 1123f, 1679</sup> Recently the latter method has become of interest.<sup>542, 1687, 1883</sup> Pure melamine may be prepared by heating fused ammonium thiocyanate with dilute hydrochloric acid.<sup>1472c</sup>

Dropping a solution of ammonium thiocyanate onto a nickel surface heated to 250° gives carbon disulfide, ammonia, hydrogen sulfide, and carbon dioxide.<sup>663b, 664, 739</sup> Heating with water at 200° under pressure hydrolyzes ammonium thiocyanate:<sup>738</sup>



Ammonium thiocyanate heated with sulfuric acid and ammonium sulfate is converted to ammonium sulfate.<sup>738, 1354</sup>

Ammonium thiocyanate in aqueous solution is decomposed by ultraviolet light and by an electric discharge.<sup>629, 661, 829</sup> When a concentrated aqueous solution of  $\text{NH}_4\text{SCN}$  (above 3.5 N) is exposed to sunlight, a color appears in about 10 seconds. A colored compound is precipitated in about five hours. The same precipitate is formed in the presence of  $\text{H}_2\text{O}_2$  and other oxidising agents. The reaction appears to be the oxidation of thiocyanic acid to thiocyanogen, which polymerizes.<sup>153</sup>

When ammonium thiocyanate is heated to 180° C. ammonium trithiocarbonate sublimes out and guanidine thiocyanate is left as a residue. The over-all reaction is:



The intermediate steps are not known, but it is probable that the salt is first isomerized to thiourea:



Guanidine salts are made by heating ammonium thiocyanate and an oxide or salt of a heavy metal with ammonia.<sup>671a</sup> Guanidine is prepared by the interaction of dicyano-diamide and ammonium thiocyanate.<sup>1868</sup> Ammonia passed through molten ammonium thiocyanate forms guanidine thiocyanate.<sup>641, 660</sup> Alkylene diguanidine thiocyanates of high molecular weight are

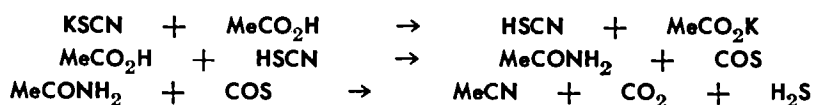
obtained by heating alkylene diamines of high molecular weight with guanidine thiocyanate.<sup>1480</sup>

Sulfur monochloride reacts with a metal thiocyanate:<sup>198</sup>

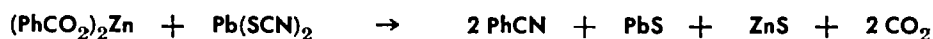


This was formerly supposed to be the disulfide,  $\text{S}_2(\text{SCN})_2$ .<sup>1089b</sup>

Potassium thiocyanate dissolved in boiling acetic acid gives acetamide, acetonitrile, carbon dioxide, and hydrogen sulfide:



With benzoic acid, the yield of benzonitrile was 80% of theory<sup>1112</sup> but this was only 40% if calculated on the total benzoic acid. From zinc benzoate and lead thiocyanate the yield of benzonitrile is high:<sup>1481a</sup>



Thiocyanic acid does not condense with aldehydes in the presence of acids but gives red colorations with aldehydes and alkali.<sup>99</sup>

Perhaps the most remarkable property of thiocyanates is the dispersion of cellulose in certain concentrations of calcium and other metal thiocyanates. It would lead too far to go into this here.<sup>1895</sup>

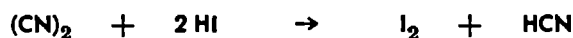
As will be shown in a later section, *gem*-dithiocyanates may be prepared in another way. Solutions of thiocyanates have a similar peptizing action on polyvinyl alcohol.<sup>1307</sup> Ash-free casein dissolves in 5 parts of a 20% aqueous solution of ammonium thiocyanate. Technical casein is conveniently titrated in a thiocyanate solution.<sup>1556</sup>

Thiocyanic acid reacts with  $\text{NOCl}$ :<sup>1628</sup>

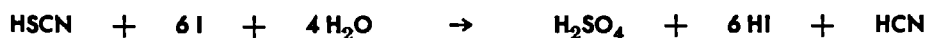


#### ESTIMATION OF THIOCYANIC ACID

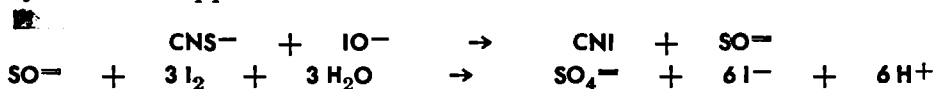
Thiocyanic acid may be determined by titration with a standard solution of an oxidising agent such as potassium permanganate,<sup>1019, 1609</sup> bromate,<sup>933b, 1299</sup> iodate,<sup>933b</sup> hypochlorite,<sup>156, 174</sup> bromine,<sup>1033, 1651</sup> or iodine chloride.<sup>347, 348, 1536, 1537</sup> In the presence of hydrochloric acid, cyanogen reacts with hydrogen iodide:



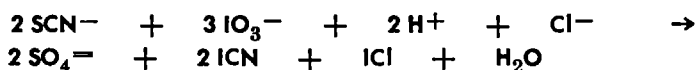
The net result is: <sup>1769</sup>



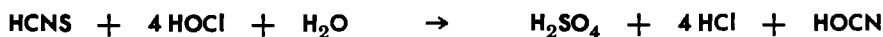
From a kinetic study of the iodometric oxidation of thiocyanates it appears that the reactions are: <sup>36</sup>



Oxidation of thiocyanate ion by iodate ion proceeds in three stages because thiocyanate ion, hydrocyanic acid, and iodine react with the iodate successively: <sup>626</sup>



An immiscible solvent to which the iodine imparts a bright color, so long as an excess of it is present, may aid. <sup>1676</sup> Hypochlorite may be used for the titration: <sup>156, 174</sup>



Thiocyanate ion may be titrated with silver nitrate <sup>1200</sup> or with mercuric nitrate. <sup>189</sup> Thiocyanate ion can be determined coulometrically down to 0.5  $\gamma$   $\text{SCN}^-$  with an error of about 0.3%, <sup>1297, 1734</sup> or to 0.1  $\gamma$  by the formation of complexes containing certain organic nitrogen bases, <sup>1201</sup> even in the presence of  $\text{I}^-$  and  $\text{ACO}^-$ . <sup>1057</sup> Methods have been derived for the electrochromatographic determination of thiocyanate ions. <sup>6, 1293</sup> The electrophoresis of the thiocyanate ion is 20% faster than that of the chloride ion. <sup>700</sup>

In a micro-method, reliance is put upon the fact that cyanogen bromide develops a deep orange-red color with benzidine in pyridine. <sup>16</sup> This method may be used in the presence of glycine. <sup>844</sup>

A mercurimetric method is said to be very accurate. <sup>514</sup> A colorimetric method has been determined for the stepwise determination of chloride, cyanide, and thiocyanate <sup>884</sup> ions. An extensive comparison has been made of the indicators used in the determination of the thiocyanate ions <sup>1260</sup> and methods of determination have been reviewed. <sup>53</sup>

## SALTS OF THIOCYANIC ACID

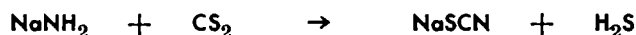
This subject is a large one but will be considered only briefly. Only a few of many references will be given.

Thiocyanates result from many reactions, some of them easily explained and others not at all understood. Whenever ammonia or alkali, sulfur, and carbon-nitrogen compounds are brought together, there is a possibility of the formation of a thiocyanate.

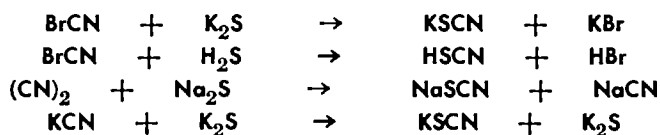
Sodium cyanide takes up sulfur with great ease, practically quantitatively:



This reaction is rapid even in cold solutions in water or alcohols but it does not take place in carbon disulfide, hydrocarbons, or chlorinated hydrocarbons, in which alkali-cyanide is not soluble.<sup>306</sup> Sodamide reacts with carbon disulfide:<sup>1902</sup>



Cyanogen and its bromide combine with potassium sulfide<sup>719a</sup> or with hydrogen sulfide:<sup>441d</sup>



When a suspension of mercury fulminate in water is treated in the cold with hydrogen sulfide and filtered, the filtrate gives the reactions of thiocyanic acid.<sup>292</sup>

Commercially, ammonium and metal thiocyanates are obtained from coke-oven gases. There are many patents on methods of operating and purification, only a few of which are given here.<sup>404, 604, 640, 664, 670, 1328, 1759</sup> An emulsifier is useful to effect a reaction between aqueous ammonia and ammonium sulfide and carbon disulfide.<sup>632</sup> Waste gases from the soda-cellulose process are said to have been used.<sup>1321</sup> Calcium cyanamide may be heated with sulfur, with or without alkali, or with carbon disulfide.<sup>269, 776</sup> Heating formamide, ammonia, and sulfur is said to produce ammonium thiocyanate.<sup>1621</sup>

Betaine thiocyanate is prepared by treating betaine with thiocyanic acid<sup>142</sup> or by double decomposition from betaine hydrochloride and ammonium thiocyanate.<sup>142, 856, 858, 859</sup> Thiocyanates

of pyridine and quinoline betaines are obtained from the corresponding quaternary bases.<sup>944</sup> Useful quaternary ammonium thiocyanate derivatives are made by reaching a halogenated thiocyanate, such as  $\text{ClCH}_2\text{CH}_2\text{SCN}$ , with a tertiary amine.<sup>1279</sup>

Phosphorus trichloride and potassium thiocyanate, in ethanol solution, give a compound of the formula  $\text{C}_8\text{H}_{18}\text{N}_4\text{S}_4\text{O}$ .<sup>1140</sup> Several methods have been claimed for the production of guanidine thiocyanate; *viz.*, from ammonia and carbon disulfide in a closed reaction zone,<sup>24, 1195, 1196</sup> from urea and hydrogen sulfide under pressure,<sup>1195</sup> and from carbon oxysulfide and ammonia under pressure.<sup>1196</sup>

The familiar red ferric thiocyanate—a test for ferric or for thiocyanate ions—has received much attention.<sup>88, 392, 738, 1256, 1404a</sup>

Complex thiocyanic salts containing two or more metals are known in considerable variety. In some cases organic bases are involved. There is a review by Babko,<sup>72</sup> with 113 references, of thiocyanate complexes of metals, including their properties in solution, formation, dissociation equilibrium, color, and stability. Their relations to halogen complexes is briefly discussed. Thiocyanate complexes of the following elements have been reported, and properties such as crystal structure, stability, absorption spectra, conductivity, and color have been studied: iron,<sup>72, 136, 273, 372, 689, 902, 1086, 1353, 1390, 1489, 1490, 1618, 1922</sup> copper,<sup>89, 273, 291, 648, 649, 678, 902, 1153, 1352, 1695, 1700</sup> cobalt,<sup>3, 4, 20, 63, 73, 103, 188, 300, 584, 601, 720, 877, 1083, 1113, 1119, 1201, 1345a, 1345b, 1426, 1439, 1475, 1700, 1816, 1871, 1919, 1938, 1939</sup> mercury,<sup>291, 419, 618, 1043, 1192, 1345a, 1345b, 1622, 1662, 1732, 1957, 1958</sup> nickel,<sup>122, 273, 689, 902, 1144, 1475, 1937</sup> zinc,<sup>273, 680, 720, 1475, 1700, 1957</sup> cadmium,<sup>273, 679, 720, 849, 1144, 1345a, 1345b, 1475, 1700, 1799, 1806, 1957</sup> manganese,<sup>273, 1475, 1921</sup> bismuth,<sup>295, 617, 1002, 1345a, 1345b, 1357</sup> tungsten,<sup>1797</sup> uranium,<sup>11</sup> chromium,<sup>54, 106, 123, 175, 1407, 1626, 1925</sup> rhodium,<sup>1957</sup> niobium,<sup>76, 762, 1797</sup> thallium,<sup>270, 295</sup> platinum,<sup>327, 1542, 1919</sup> palladium,<sup>270, 327, 1135, 1542, 1919</sup> lead,<sup>681, 1109, 1345a, 1345b</sup> silver<sup>678, 1643</sup> and rhenium.<sup>1751</sup>

The exchange reaction between chromium (III) thiocyanate complex and free thiocyanate ion in aqueous solution was studied at 30–60° by using  $\text{S}^{35}$ .<sup>999</sup> The distribution of electron density in the thiocyanate ion has been determined by crystallochemical analysis of the nature of the chemical bonds in the complex metal thiocyanates.<sup>1957</sup>

Certain thiocyanate complexes have been found useful in the determination of: ferrous<sup>1150</sup> and ferric ions<sup>1338, 1410</sup> iron in water,<sup>282</sup> and also for the separation of ferric iron from aluminum;<sup>1942</sup> the microestimation of copper;<sup>496b</sup> the determination of copper in the presence of various ions;<sup>785</sup> the thiocyanate-cerimetric determination of silver and copper;<sup>933a</sup> the separation of copper from molybdenum;<sup>1692</sup> the spectrometric determination of cobalt;<sup>273, 1655, 1944</sup> the amperometric titration of zinc, cobalt, and copper with potassium mercury tetrathiocyanate;<sup>995</sup> the detection of cobalt with alkali thiocyanate and tributylamine;<sup>1942</sup> the colorimetric micro-determination of zinc,<sup>1197</sup> cobalt<sup>496a, 871</sup> and molybdenum;<sup>1561</sup> the microchemical determination of silver;<sup>267</sup> the volumetric determination of cerium;<sup>423</sup> the precipitation of mercurous salts as  $\text{Hg}_2(\text{SCN})_2$ ;<sup>276</sup> the determination of palladium as  $\text{PdCl}_2 \cdot 2\text{RNH}_2$  complex;<sup>1450</sup> qualitative tests for zinc<sup>173, 190</sup> and osmium;<sup>98</sup> and the potentiometric determination of iron.<sup>1943</sup> Aminopyrine and antipyrine give characteristic reactions with complex thiocyanates of cobalt, zinc, and nickel.<sup>273</sup> Bivalent metal thiocyanates of manganese, cobalt, nickel, cadmium, and zinc form complexes with thiourea.<sup>1300</sup>

Titanium gives a variety of salts with thiocyanic, perthiocyanic, and trithiocyanuric acids. Some of these involve organic bases.<sup>1520</sup> Certain metal thiocyanates form etherates:



The molecular polarization<sup>628</sup> and polar moment,<sup>628</sup> conductivity in aqueous solution,<sup>605</sup> and lowering of freezing point in benzene<sup>106</sup> of tetra-*i*-amylthiocyanate have been studied. The conductivities of tetramethylammonium thiocyanate in non-aqueous solvents have been determined.<sup>1847</sup> A tetra-alkylammonium thiocyanate decomposes at 210° C. into a tertiary amine and an alkyl isothiocyanate:<sup>1238</sup>



The reaction rates of thiocyanate ion with trityl, *p,p'* dimethyl benzhydryl, benzhydryl, and *tert*-butyl ions,<sup>1731</sup> and with  $\text{Me}_3\text{PO}_4$ , dimethyl ethyl phosphonate and dibenzyl methyl phosphonate<sup>843</sup> have been compared. The influence of thiocyanate ion on the rate of evolution of nitrogen from the azide ion-iodine

system has been determined under varying conditions.<sup>1635</sup> In the decomposition of diazoacetic ester, thiocyanic acid is about as powerful as hydriodic.<sup>828a</sup>

It was found that the binding of thiocyanate ions to insulin is independent pH.<sup>1619</sup>

Sodium thiocyanate in soil hinders the oxidation of ammonium nitrogen to nitrate nitrogen, and of nitrite N to nitrate N.<sup>657</sup>

Eutectics have been observed in the systems of sodium and potassium thiocyanates and formates.<sup>1688</sup> The conductivities of solutions of allylaniline thiocyanate in methyl and ethyl alcohols and in aqueous dioxane have been measured.<sup>1004</sup>

### Thiocyanogen

Thiocyanogen,  $(\text{SCN})_2$ , resembles the halogens in many of its reactions and has been called a *pseudohalogen*. Its chemistry has been summarized by Wood, Kaufman,<sup>1908</sup> and others.<sup>355, 958, 959, 960</sup>

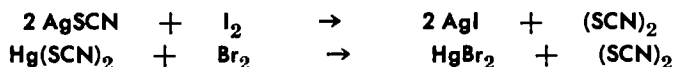
On account of its tendency to polymerize, little is known of the properties of thiocyanogen in the free state. When a carbon disulfide solution of it is cooled to  $-70^\circ$ , nearly colorless crystals, melting at  $-2^\circ$ , separate. When warmed to room temperature, these polymerize with the evolution of smoke leaving an amorphous red mass.<sup>1685</sup> Similar results have been obtained by evaporating solutions of thiocyanogen in ethyl chloride, ethyl bromide, or ether, over sulfuric acid.<sup>1848</sup> As thiocyanogen is easily polymerized under the catalytic influence of heat, light, or moisture, it is usually prepared in an organic solvent and used immediately. In a dry non-polar solvent thiocyanogen is relatively stable. In a one-tenth normal solution in carbon tetrachloride at room temperature, polymerization is 50% in twenty-four hours in the sunlight, but only 5% in the dark.<sup>972</sup>

Thiocyanogen may be generated by the electrolysis of concentrated aqueous solutions of alkali thiocyanates.<sup>337, 775, 974, 993, 1228, 1230, 1316, 1512</sup> The temperature should be kept below  $-8^\circ$ , ethanol being added to prevent freezing, and the concentration of thiocyanogen maintained below that of the complex  $\text{NH}_4(\text{SCN})_3$ . Lignin sulfonic acid is said to be thiocyanated by thiocyanogen generated electrolytically.<sup>1614, 1615</sup>

Thiocyanogen may also be liberated from thiocyanate salts by chemical reagents, as when bromine or chlorine is added to a

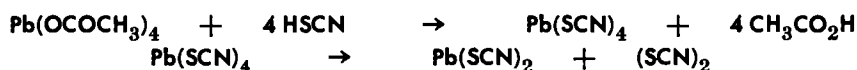


solution of a metal thiocyanate<sup>788, 835, 856, 858, 859, 861, 865a, 958, 959, 960, 965, 972b, 976, 979, 983, 1685, 1929</sup> in acetic or formic acid<sup>974, 1929</sup> or when iodine or bromine is added to a suspension of silver-,<sup>862</sup> lead-, or mercury thiocyanate in an anhydrous, non-polar liquid.<sup>958, 959, 960, 983</sup>

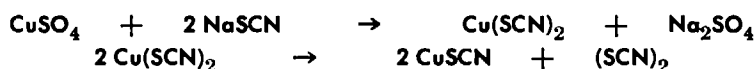


The chlorine may come from compounds in which it is loosely bound, such as sulfonyl chloride,<sup>15, 868, 1693</sup> dichlorourea,<sup>1129</sup> dichloropentamethylenetetramine,<sup>1127</sup> and phenyl iodosochloride.<sup>1316</sup>

Lead tetrathiocyanate, from lead tetraacetate and thiocyanic acid, sets free thiocyanogen:<sup>970a</sup>



The thiocyanogen may come from the decomposition of cupric thiocyanate which is readily prepared from a thiocyanate and a cupric salt:



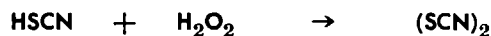
The cupric thiocyanate may be precipitated, filtered off, and dried before use; or the organic compound to be thiocyanated may be mixed with a cupric salt in methanol, or in water, and sodium thiocyanate then added.<sup>356, 945, 958, 959, 960, 971, 1187</sup> The decomposition of cupric thiocyanate may be considerably more complicated than is represented by the preceding equation.<sup>1404b</sup>

A small yield of thiocyanogen is obtained by treating an ether solution of thiocyanic acid with manganese dioxide. This may be considered to be analogous to a well known method for preparing chlorine.<sup>970a</sup>

Thiocyanogen is a decomposition product of azido-carbon disulfide:<sup>250</sup>

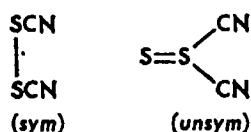


Thiocyanic acid is oxidised to thiocyanogen by hydrogen peroxide:<sup>1403.4</sup>



The molecular weight of thiocyanogen, determined cryoscopically, corresponds to  $(\text{SCN})_2$ .<sup>1089a</sup> The solution potential of

thiocyanogen is 0.769 volts which is between those of iodine, 0.54, and bromine, 1.09.<sup>176</sup> The constitution is believed to be  $\text{N}:\text{C}\cdot\text{S}\cdot\text{S}\cdot\text{C}:\text{N}$ ; the  $-\text{S}\cdot\text{S}-$  bond is homopolar.<sup>1093</sup> In view of the fact that the polymerization of thiocyanogen has been found to take place with formation of small quantities of cyanogen thiocyanate and dithiocyanogen mono-sulfide, it has been assumed that the halogenoid is capable of existing in two tautomeric forms, *viz.*:<sup>970a</sup>



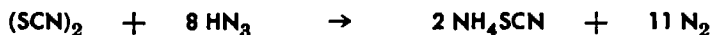
Thiocyanogen in a freshly prepared solution is diamagnetic but, on standing, turns yellow and becomes paramagnetic. Its polymerization has been followed by measuring the magnetic susceptibility.<sup>154</sup>

Solutions of thiocyanogen in non-polar organic solvents, like those of halogens, do not conduct electricity.<sup>536</sup>

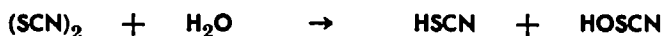
#### REACTIONS OF THIOCYANOGEN

On account of its instability and the difficulty of isolating it, thiocyanogen is generated in the solvent in which it is to be used. The solvent should be one in which the organic compound is soluble and in which the thiocyanate salt can be either dissolved or suspended, and the temperature should not be above 20° C.<sup>788, 835, 856, 858, 859, 861, 865a, 958, 959, 960, 965, 972b, 976, 979, 983, 1685, 1929</sup> It is said to be desirable to protect methanol and similar solvents from attack by thiocyanogen by saturating them with salts such as sodium chloride or bromide.<sup>865b</sup>

Thiocyanogen is converted to ammonium thiocyanate by hydrazoic acid:<sup>1887</sup>



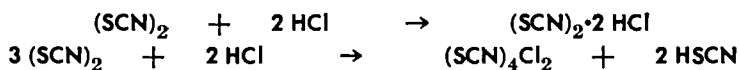
If thiocyanogen should react with water as bromine does, we would have:



If HOSCN is formed, it must undergo some further reaction. The products isolated correspond to: <sup>176, 666, 970b, 1089b</sup>



Thiocyanogen combines with hydrogen chloride: <sup>1686</sup>

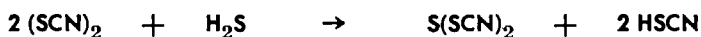


and with chlorine:



Some of the trichloride is also formed. The monochloride, evidently a polymer,<sup>38, 958, 959, 960, 972c, 1092</sup> is an odorless solid which decomposes around 200°. Thiocyanogen iodide has not been isolated but it seems to be formed by the action of iodine on silver thiocyanate, or by the addition of iodine to thiocyanogen in solution.<sup>167, 168, 169, 967a</sup> As will be mentioned later, solutions supposed to contain thiocyanogen iodide have been used for the determination of thiocyanogen numbers.

Thiocyanogen reacts with hydrogen sulfide: <sup>1094</sup>

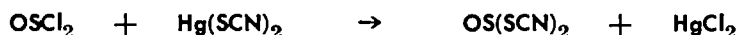


The product from mercuric thiocyanate and sulfur monochloride was supposed to be the disulfide,<sup>1089b</sup> but has since been found to be a mixture: <sup>198</sup>

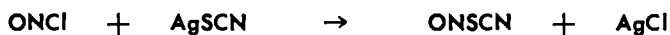


This sulfide can be made by heating dry potassium thiocyanate with sulfur chloride.<sup>246</sup> Thiocyanogen diselenide,  $\text{Se}_2(\text{SCN})_2$ , and the mixed  $\text{SSe}(\text{SCN})_2$  have been prepared.<sup>102</sup> The monosulfide, a solid, insoluble in water and stable up to 500°, is evidently a polymer.

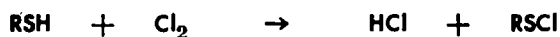
Thiocyanogen sulfoxide, from thionyl chloride and mercuric thiocyanate in carbon disulfide, is an orange-red amorphous powder: <sup>1177</sup>



The reaction between nitrosyl chloride and silver thiocyanate has been supposed to give nitrosylthiocyanogen; however, the product has not been isolated.<sup>1090</sup>



Sulfen chlorides,  $-\text{SCl}$ , are formed by the reaction of chlorine with a mercaptan:

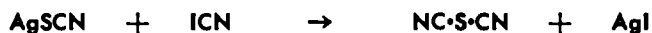


Sulfen thiocyanides are formed similarly: <sup>1093, 1094</sup>

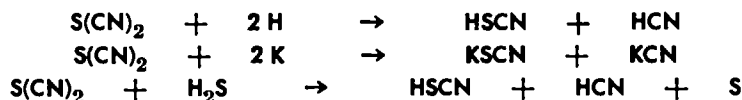


The thiocyanides are considerably more stable than the corresponding sulfen chlorides. The reactions of the two groups are much the same; see Vol. I, Chapter 3, where they are treated more fully.

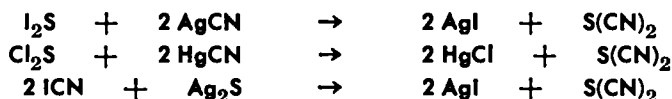
Cyanogen iodide reacts with silver thiocyanate:



The thiocyanogen cyanide, or cyanogen sulfide,  $\text{S}(\text{CN})_2$ , is a solid, m.  $60^\circ$ , subliming at  $30\text{--}40^\circ$ . It is decomposed by water into a mixture of products. It reacts with many reagents: <sup>1132</sup>



Cyanogen sulfide can be obtained otherwise: <sup>1132</sup>



Thiocyanogen reacts with ammonia:



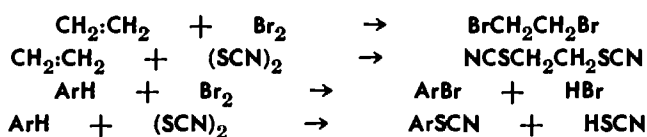
This rhodanamine is an unstable oil. The compounds from dialkyl amines such as  $\text{Et}_2\text{NSCN}$  are more stable. Analogous compounds, such as  $\text{EtONEtSCN}$ , can be obtained from hydroxylated amines. <sup>929, 1092, 1095</sup> Thiocyanogen can add to a triaryl derivative, such as triphenyl stibine <sup>323</sup> and triphenyl bismuthine: <sup>324</sup>



The reaction of thiocyanogen with azide ions has been investigated. <sup>93</sup> Free thiocyanogen adds to trivalent phosphorous compounds, such as esters of acids of trivalent phosphorus, dialkyl phosphites, and dialkyl thiophosphites. <sup>1243</sup>

Thiocyanogen derivatives are obtained by the reaction of cyanogen chloride with a metal xanthate or dithiocarbamate. <sup>1681</sup>

Thiocyanogen, a pseudohalogen, imitates but does not equal the real halogens in its reactions of addition to unsaturates and substitution with aromatics: <sup>422, 958, 959, 960, 974, 1052</sup>

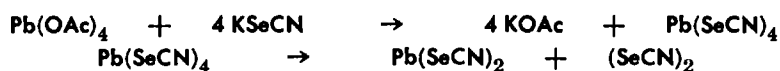


The applications of these reactions to the preparation of thiocyanates will be considered in a later section. Thiocyanogen is selective in its addition to double bonds, adding completely to some and not at all to others; for example, it does not combine with maleic, fumaric, acrylic, crotonic, and cinnamic acids.<sup>958, 959, 960</sup> Only certain double bonds of the steroids take up thiocyanogen; those in the 4,5, and 2,2 positions do not.<sup>1704</sup> Abietic acid takes up thiocyanogen corresponding to one double bond. In benzene at 0°,  $\alpha$ -pinene,  $\beta$ -pinene and terpinolene react to the same extent. Camphene adds thiocyanogen very slowly, and dipentene scarcely at all.<sup>732</sup> A catalyst such as mercuric chloride accelerates the addition of thiocyanogen to the double bonds of unsaturated oils, and at the same time retards polymerization of the reagent.<sup>317</sup>

The addition products and substitution products are said to be useful in preparations.

The percentage of thiocyanogen taken up by an unsaturate is known as its *thiocyanogen number*. All of this will be considered at length in a later section.

The analogous selenocyanogen,  $(\text{SeCN})_2$ , has been prepared by the reaction of lead tetraacetate with potassium selenocyanate in acetone:



Selenocyanogen is hydrolyzed by water with the formation of selenious, hydrocyanic, and selenocyanic acids.<sup>970b</sup>

### THIOCYANOGEN NUMBERS

As is well known, iodine numbers are extensively used for the characterization and identification of vegetable and animal oils. The iodine number is defined as the number of milligrams of iodine taken up by 100 mg of the oil. Oleic acid has the molecular weight 282, hence 282 mg of it should take up 254 mg of iodine,

from which we can calculate the theoretical iodine number 92. Oleic acid takes up the equivalent amount of thiocyanogen, 116 mg, for 282 mg of oleic acid, or 42 mg for 100 mg of the acid. As thiocyanogen solutions are titrated iodometrically in the presence of potassium iodide, the thiocyanogen is reported as iodine. Thus the 116 mg of thiocyanogen, taken up by a molecule of oleic acid is reported as 254 mg of iodine, which makes the thiocyanogen number 92—the same as the iodine number. For determining the unsaturation of an oil, it makes no difference whether the addendum is thiocyanogen or iodine, as both are determined by the same titration. The manner of determining the thiocyanogen number is similar to that of the iodine number;<sup>621, 684, 958, 959, 960, 962, 965, 967c, 968, 969, 970b, 972b, 980, 982, 1835, 1888</sup> that is, a moderate excess of standard thiocyanogen solution is added to a weighed sample of the oil and the excess is titrated in the presence of potassium iodide.

For oleic acid, in which there is one double bond, the iodine and thiocyanogen numbers are the same. For linoleic acid, however, there is a marked difference; iodine adds to both double bonds, whereas thiocyanogen adds to only one. Thus, the thiocyanogen number is 92, but the iodine number is 184. This makes it possible to estimate the relative amounts of these two acids in a mixture. In a mixture of stearic, oleic, and linolenic acids, and a mixture of  $x$ ,  $y$ , and  $z$ , respectively, we have  $x + y + z = 100$ ,  $92(y + z) = \text{thiocyanogen number}$ , and  $92y + 184z = \text{iodine number}$ . Having three equations we can solve for  $x$ ,  $y$ , and  $z$ .

For olive oil, the thiocyanogen number is 76.5, compared with an iodine number of 80.8; and for cottonseed oil the thiocyanogen number is 67.3, compared with an iodine number of 111.<sup>958, 959, 960</sup> From these figures we can compute the predominance of oleic acid in olive oil, and of linoleic acid in cottonseed oil. The determination of both the iodine and the thiocyanogen numbers serves to differentiate between the two oils.<sup>52, 61, 288, 665, 701, 795, 807, 882, 953, 958, 959, 960, 963, 969, 973, 1001d, 1209, 1234, 1249, 1496, 1851</sup> It is assumed in the preceding that only oleic and linoleic acid are present. A molecule of linolenic acid, which has three double bonds, takes up more than one molecule of thiocyanogen but less than two.<sup>97, 1001c, 1049, 1698a</sup>

The thiocyanogen number has been used in the study of the hardening of fats<sup>1808</sup> and the drying of oil films.<sup>303</sup> In the hydro-

generation of lard, it has been found that 73.7% of the linoleic acid has disappeared when the sum of the unsaturated acids has been reduced by only 1.3%.<sup>1932</sup>

The thiocyanogen and iodine numbers of fish oils<sup>1789a, 1808</sup> and of 62 Netherlands butters<sup>1282</sup> have been recorded. The oil from seeds of *Euphobia Cathyris* has an iodine number 81.7–84.9, and a thiocyanogen number, 68.0–69.1.<sup>1540</sup>

Rubber takes up thiocyanogen quantitatively. The titration must be done quickly if secondary reactions are to be avoided.<sup>355, 1453</sup>

#### DETERMINATION OF THIOCYANOGEN NUMBER

Various procedures have been recommended for preparing the standard thiocyanogen solution.<sup>288, 367c, 622, 732, 740, 848, 958, 959, 960, 1080, 1175, 1224b, 1336, 1360, 1462, 1479, 1654, 1698b, 1873</sup>

As with iodine, acetic acid is the usual solvent, but with the difference that the acetic acid must be really anhydrous because water in the solution causes decomposition. A small amount of acetanhydride, judged to be sufficient to take care of the water that may be present, is added to ordinary acetic acid and the mixture is heated. To the cooled acetic acid a slight excess of lead thiocyanate is added and the calculated amount of dry bromine is added to the suspension. After agitation, the lead bromide and the residual lead thiocyanate are filtered off and the solution is standardized with thiosulfate in the presence of potassium iodide. The solution is not so stable as the corresponding iodine solution.

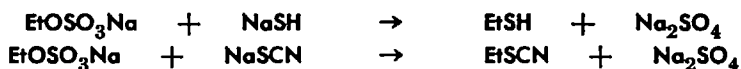
As with neither thiocyanogen or iodine is the addition complete, and as with both there may be some substitution, to obtain comparable results it is necessary that the determinations be made under precisely specified conditions.<sup>635</sup> When this injunction is followed, strictly comparable results are obtained. As a test of the method, the thiocyanogen number of a sample of cottonseed oil was determined in six different laboratories; the average value was 67 with a maximum variance of 0.3.<sup>1224a</sup>

As solutions of thiocyanogen, even under the best of conditions, are not so stable as might be desired, a study has been made of thiocyanogen iodide, ISCN, as a possible substitute. The same solvents are used for this as for thiocyanogen. When properly made, its solutions are quite stable and determinations can be made with it in the usual way. Unfortunately, the addition does

not stop short at one double bond, though it does slow down.<sup>987a, 987b</sup>

### Thiocyanic Esters

Zeise's excellent results in the preparation of ethyl mercaptan by distilling a mixture of sodium ethyl sulfate and sodium hydrosulfide led him to try to make ethyl thiocyanate similarly:



Unfortunately, the conditions that were satisfactory for mercaptans were too severe for the less volatile and more sensitive thiocyanates.

Liebig<sup>1123c</sup> attempted to prepare an alkyl thiocyanate by distilling a mixture of ethanol, potassium thiocyanate, and sulfuric acid, but obtained no definite results. Cahours<sup>286a</sup> distilled a mixture of concentrated solutions of potassium thiocyanate and methyl calcium sulfate and obtained methyl thiocyanate; he prepared ethyl thiocyanate similarly.<sup>286a, 1290</sup> Isoamyl thiocyanate was obtained by distilling a mixture of crystalline potassium,<sup>781</sup> or calcium<sup>1220</sup> isoamyl sulfate and potassium thiocyanate from a retort.

Some ethyl thiocyanate was obtained when an aqueous alcohol solution of potassium thiocyanate was acidified with sulfuric acid and distilled.<sup>786</sup>

### PREPARATION OF THIOCYANATES

#### *General Method*

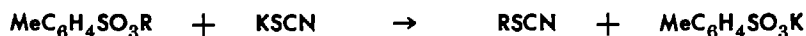
The most generally applicable method of preparing alkyl thiocyanates is the reaction of an alkyl halide or sulfate with a metal thiocyanate. In some cases isothiocyanates are obtained. In one experiment the product from *t*-butyl chloride and ammonium thiocyanate was 78% *t*-butylthiocyanate and 22% *t*-butyl isothiocyanate.<sup>1584</sup>

Arylaliphatic halides may be used but the aryl do not react unless activated by groups such as the nitro group. Diazonium halides react satisfactorily:





*p*-Toluenesulfonates, particularly of the higher alcohols, are convenient for the preparation of alkyl thiocyanates:<sup>507</sup>



Cholesteryl-*p*-toluenesulfonate<sup>110, 1280</sup> and tosylated sugars<sup>1281</sup> have been used in this way. Refluxing  $\text{PhSO}_3\text{C}_6\text{H}_3(\text{NO}_2)_2$ -2,4 with potassium thiocyanate gives 2,4-( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3\text{SCN}$ .<sup>1825, 5</sup>

The sulfonate group of 4-chlorobutylmethane sulfonate is more easily substituted than is the halogen:<sup>1378</sup>



With the nitrate it is the halogen that is substituted.<sup>1378</sup>

The lower alkyl thiocyanates, such as methyl,<sup>813, 814</sup> ethyl,<sup>1506</sup> and *i*-butyl,<sup>817</sup> may be separated from the reaction mixtures by careful distillation, but the higher ones have to be isolated in other ways. The usual solvents are water,<sup>388</sup> ethanol,<sup>21, 94, 111, 193, 388, 690, 779a, 856, 858, 859, 897, 956, 1128, 1240, 1241a, 1386, 1517, 1579, 1658, 1697, 1813, 1877a, 1877b 1877c, 1878a</sup> and acetone, in which ammonium, potassium, and sodium thiocyanates are fully soluble. The boiling point of the solvent should not be near that of the product to be isolated. Water serves well for the reactions with the sodium alkyl sulfates and for the more reactive dimethyl and diethyl sulfates, which are preferred since they became available.<sup>956</sup> Detailed directions for the preparation of methyl thiocyanate using dimethyl sulfate have been given.<sup>647a, 1847</sup> Certain sodium alkyl sulfates may be prepared by neutralizing the addition products of sulfuric acid to unsaturates.<sup>1097</sup>

For the alkyl halides, ethanol is substituted for part or all of the water. Sunlight has been found to accelerate the reactions with alkyl chlorides.<sup>1142a, 1573a</sup> A great variety of halides have been used for the preparation of thiocyanates. Among these are:  $\alpha$ -furfuryl chloride,<sup>1005</sup>  $\beta$ -naphthylmethyl chloride,<sup>1509</sup>  $\beta$ - $\beta'$ -dibromoethyl sulfide,<sup>1707</sup> *o*-nitropiperonyl chloride,<sup>1890</sup> 6-chloropyrimidines,<sup>338, 339, 921, 924</sup> acetobromocellobiose,<sup>172</sup> acetobromoglucose,<sup>543b, 1889</sup> 2-hydroxy-3,5-dibromobenzyl bromide,<sup>69a, 70, 1709</sup> and diphenylcarbamyl chloride.<sup>920</sup> Triphenylmethyl thiocyanate can be obtained from triphenylmethyl chloride and potassium thiocyanate;<sup>157, 1128</sup> and also from this chloride and free thiocyanic acid, as has been mentioned in a previous section.

Thiocyanic acid reacts with chloroacetic acid to give thiocynoacetic acid.<sup>1314</sup>

An ester of chloroacetic acid reacts readily with a metal thiocyanate to give the corresponding thiocyanic ester: <sup>772, 1020, 1533b, 1875</sup>

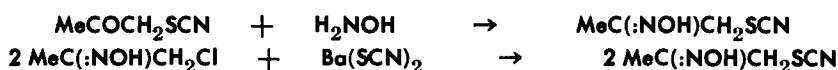


The same is true of the esters of other halogenated acids such as  $\alpha$ -chloropropionic.<sup>25, 147, 758, 1875, 1956</sup> Thiocyanomalonic ester  $(\text{EtO}_2\text{C})_2\text{CHSCN}$ , has been prepared from the corresponding chloroester.<sup>1874</sup> A number of thiocynoacetic esters of higher alcohols and cholesterol<sup>205b, 502, 770</sup> have been prepared in this way. The required chloracetic esters of terpene alcohols have been obtained by the addition of chloracetic acid to terpenes.<sup>203</sup>

In general, dihalides<sup>234, 268a, 268b, 289a, 414a, 414b, 658a, 658d, 728, 1000, 1110, 1690, 1878b, 1928</sup> give the corresponding dithiocyanates. This is true even when the two halogens are on the same carbon atom as in the preparation of *gem*-dithiocyanates,  $\text{CH}_2(\text{SCN})_2$ ,<sup>1110, 1878b, 1568b, 1661</sup>  $\text{CH}_3\text{CH}(\text{SCN})_2$ ,<sup>1568b</sup> and  $\text{PhCH}(\text{SCN})_2$ .<sup>1568b</sup> 1,3,5- $\text{CH}_3\text{C}_6\text{H}_2(\text{SCN})_3$ <sup>157</sup> has been prepared from 1,3,5- $\text{CH}_3\text{C}_6\text{H}_2(\text{Cl})_3$ . With propylene iodide, the product is allyl isothiocyanate, one molecule of hydriodic acid having been split off.<sup>1954</sup> When both chlorine and bromine are present, as in ethylene chlorobromide,<sup>415, 899a, 899b, 899d, 899f, 899g</sup> 1-bromo-2-chloropropane, and 1-chloro-2-bromopropane, the bromine reacts preferentially,<sup>414a</sup> and chloro-thiocyanates are formed.

In the absence of solvents, insoluble thiocyanates may react with halides, such as methyl<sup>956</sup> and ethyl<sup>1240, 1241a</sup> iodides, tetra-acetylsalicin bromide,<sup>1889</sup> iodoacetaldehyde,<sup>331</sup> and acetobromoglucose.<sup>543b, 1889</sup>

Thiocyanoketones have been of interest because they are readily converted into substituted thiazoles.<sup>43, 743, 744, 856, 858, 859</sup> It is not necessary to use a solvent; chloroacetone and barium thiocyanate and glass marbles may be shaken together.<sup>1759</sup> Chloroacetone stirred for 10 hours with a concentrated aqueous solution of sodium thiocyanate gives a good yield.<sup>1759</sup> The oxime of acetonyl thiocyanate may be prepared in two ways:<sup>1423</sup>



It occurs in two forms, one melting at  $135^\circ$  and the other at  $170^\circ$ .<sup>1423</sup>

Barium thiocyanate added to 21-chloro-4-pregnene-3,20-dione gives the 21-thiocyanato derivative.<sup>1461,5</sup>

Alkali thiocyanates react well with dichloro- as well as with monochloro-ketones, preferably in solvents such as ethanol or acetone.<sup>1322, 1568c</sup> If there is a hydroxylated alkyl on the same carbon atom as the *alpha*-halogen, the thiocyanated ketone can be converted to a 2-hydroxythiazole.<sup>26</sup> Dichloroacetone may react in two stages: <sup>1422</sup>



Refluxing NaSCN with  $\text{ClCH}_2\text{SiMe}_3$  in 96% ethanol gave 84%  $\text{Me}_3\text{SiCH}_2\text{SCN}$ .<sup>1248</sup>

Ethylene diselenocyanate and several  $\alpha$ -selenocyanic acids have been made by the same methods as the corresponding thiocyno compounds.<sup>567a, 1447</sup>

#### *Addition of Thiocyanic Acid to Unsaturation*

Thiocyanic acid, a pseudohalogen acid, can be added to unsaturates <sup>261b</sup> such as  $\beta$ -pinene,<sup>323</sup> isobutylene, trimethylethylene, pentene-2, styrene, and camphene.<sup>997</sup> With isobutylene, the product is one third *t*-butyl thiocyanate and two thirds *t*-butyl isothiocyanate. With dicyclopentadiene, only the *iso*- is formed.<sup>265</sup> The rate of addition of thiocyanic acid from solutions of KSCN to dimethyl acetylene dicarboxylate and some other triple-bonded compounds has been studied. That  $\text{SCN}^-$  adds more rapidly than  $\text{I}^-$  may be due to the smaller radius of the terminal atom.<sup>1349</sup> Rhodanopene is formed by the addition of thiocyanic acid to vinylacetylene:



This polymerizes spontaneously.<sup>1048</sup> Thiocyanic acid is said to combine with a fatty alcohol sulfinic acid.<sup>1860</sup>

Methylvinylketone treated with ammonium thiocyanate and sulfuric acid in water gives 1-thiocyanato-3-butanone.<sup>1286,6</sup>

#### *Addition of Thiocyanogen*

The reactions of thiocyanogen on organic compounds have been reviewed by Kaufmann<sup>958, 959, 960</sup> Wood,<sup>1908</sup> and by Clayton and Bann.<sup>355</sup> Thiocyanogen, a pseudohalogen, adds to a double bond

much as bromine would. The utilization of this for determining thiocyanogen number has been considered in an earlier section. The same reaction is useful for preparing vicinal thiocyanates. With ethylene, the addition goes scarcely at all in the dark, but in sunlight it is complete in several hours.<sup>262, 1684, 1685</sup> There is some polymerization of the thiocyanogen but not enough to interfere with the addition reaction. Its reaction with other olefins is more or less similar. Some metals are said to catalyze the reaction. The solvent may influence the rate;<sup>211</sup> the addition of  $(\text{SCN})_2$  to diisobutylene is rapid in benzene but slow in ether.<sup>211</sup> Vicinal dithiocyanates have been prepared from styrene, allyl alcohol, anethole, isosafrol,<sup>958, 959, 960, 972, 974</sup> cyclohexene,<sup>168</sup> 3-methyl cyclohexene,<sup>422</sup> 2-methyl cyclohexene,<sup>1271a</sup> 4-methyl cyclohexene,<sup>1271a</sup> 2-ethylcyclohexene,<sup>1271a</sup> 2-propylcyclohexene,<sup>1271a</sup> 1,4-dihydronaphthalene,<sup>1271a</sup> terpenes,<sup>204</sup> cycloolefins fused with an aromatic ring,<sup>1701</sup> diisobutylene,<sup>211</sup> vinylnaphthalenes,<sup>1701</sup> butene-2,<sup>1128</sup> and 2-vinylthiophene.<sup>499.5</sup>

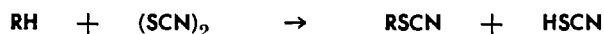
Starting with the pure acids, dithiocyanates have been obtained and characterized. Some of these are from: oleic,<sup>958, 959, 960, 1001a</sup> elaidic,<sup>82, 958, 959, 960, 967a, 1001a</sup> brassidic,<sup>824, 1001a</sup> erucic,<sup>824, 958, 959, 960, 967a</sup> petroselinic,<sup>958, 959, 960</sup> linoleic,<sup>824</sup> hydrocarpic,<sup>49a, 50</sup> dihydrohydnocarpic,<sup>49a, 50</sup> and linolenic acid.<sup>1789b</sup> Bromine, chlorine, iodine, or bromine iodide may be added to the remaining double bond of the linoleic acid.<sup>1001b</sup> The addition products may be elastic and factice-like.<sup>966</sup> Like linoleic acid, isoprene,<sup>262</sup> 2,3-dimethylbutadiene,<sup>262</sup> and butadiene<sup>955, 1277</sup> take up an amount of thiocyanogen corresponding to only one of the two double bonds. The products formed are crystalline and may be used to characterize these hydrocarbons.<sup>262</sup> That from butadiene is 1,4-dithiocyanobutene-2.<sup>955</sup>

Under the influence of light, one molecule of thiocyanogen adds to an acetylenic triple bond to form such products as  $\text{CH}(\text{SCN})\text{:CHSCN}$ , a mixture of solid *trans* and liquid *cis*.<sup>1684, 1685</sup> Addition also takes place with phenyl acetylene and  $\alpha$ -tolane.<sup>1684, 1685</sup> The rate and extent<sup>1125</sup> of addition of thiocyanogen under various conditions to acetylene and to mono- and disubstituted acetylenic hydrocarbons have been compared.<sup>1235</sup> The amount of  $(\text{SCN})_2$  taken up by rubber is reported by one observer as one  $(\text{SCN})_2$  to each  $\text{C}_5\text{H}_8$  unit,<sup>1453</sup> and by another as one-fourth of this amount.<sup>1305a</sup> Synthetic

rubbers also take up thiocyanogen.<sup>355, 1221</sup> It is claimed that the addition to natural or synthetic rubber of thiocyanogen in less than the amount needed to saturate half of the double bonds, improves<sup>80</sup> resistance to solvents without any loss of the valuable characteristics of the material.<sup>78, 79</sup> Some of the addition products are claimed to be useful.<sup>460, 1186</sup> Thiocyanogen<sup>1088</sup> and the disulfide<sup>1088, 1776</sup> are claimed as vulcanizing agents.

### *Substitution of Thiocyanogen*

Thiocyanogen imitates the real halogens, though it does not equal chlorine or bromine in its power of substitution. The typical reaction is:

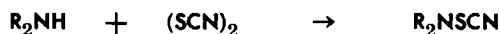


Applications of this reaction have been confined to aromatics and ketones and more narrowly to those aromatics which undergo substitution most readily such as aryl amines and phenols. The fact that thiocyanogen is unstable, particularly in high concentrations and at elevated temperatures, and in the presence of halogenation catalysts, limits its use. Substitution does not go so far as the halogens, being limited to the entry of one —SCN group<sup>958, 959, 960, 1129</sup> in the *para* position; or if that is blocked, the *ortho*, though under certain acid conditions two —SCN groups may enter.<sup>974</sup> The products are thiocyanates rather than isothiocyanates. Apparently the presence of other substituents, such as nitro, chloro, bromo, alkoxy, carboxyl, or carbethoxy groups, does not interfere with the reaction provided an active position is available. Acetic acid was the preferred solvent, but solvents such as methanol, acetone, and ethyl acetate<sup>273, 862, 958, 959, 960, 1627</sup> have been found to be preferable.

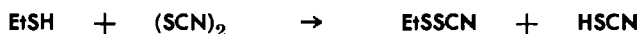
Some amines that have been thiocyanated are: aniline,<sup>864, 958, 959, 960, 974, 1129</sup> 2,5-xylylene,<sup>975</sup> *p*-toluidine,<sup>975, 1129</sup> ethyl-*p*-amino-benzoate,<sup>975</sup> sulfanilamide,<sup>964</sup> 3,4-benzopyrene,<sup>910</sup> 20-methyl cholanthere,<sup>910</sup> 1,2-benzanthracene,<sup>910</sup> N-cetyl aniline,<sup>49b</sup> N-chaulmoogryl aniline,<sup>49b</sup> N-oleylaniline,<sup>49b</sup> N,N-dimethylaniline,<sup>239, 538</sup> N,N-dimethyl-*p*-toluidine,<sup>538</sup> diphenylamine,<sup>1685</sup> benzidine,<sup>134</sup> terpenes,<sup>1277</sup> triphenylamine,<sup>1685</sup> and lignin.<sup>1615</sup> The thiocyanation of dimethylaniline is rapid, that of diethylaniline is less so, and that of dimethyl-*p*-toluidine is still less so.<sup>538, 981, 1544</sup> Diphenylamine reacts almost instantly.<sup>1332</sup> The primary thiocyana-

tion products of *p*-toluidine, *p*-nitroaniline, *p*-chloroaniline,<sup>975</sup> *p*-aminobenzoic acid, phenetidine,<sup>1316</sup> and 2,4-xylylene<sup>237</sup> are readily condensed to aminobenzothiazoles. Dithiocyano derivatives of aniline,<sup>864, 958, 959, 960, 1129</sup> *p*-toluidine,<sup>975, 1129</sup> 2,5-xylylene,<sup>975</sup> and pyrrole<sup>1431</sup> have been prepared. The open *ortho* positions in *p*-thiocyanoaniline can be taken by bromine, giving 2,6-dibromo-4-thiocyanoaniline.<sup>434</sup>

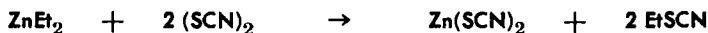
Substitution may take place in a ketone such as methyl styryl ketone.<sup>318</sup> Thiocyanogen, like bromine or chlorine, may substitute for the N-hydrogen of a primary or secondary amine: <sup>929, 1095, 1685</sup>



The S-hydrogen of a mercaptan reacts similarly:



Thiophenol and nitrophenol give analogous compounds. This has been taken up in Volume I, page 272. Thiocyanogen may be substituted for the metal atom in some organometallic compounds: <sup>1685</sup>

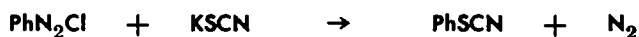


The thiocyanation of phenols has been studied less extensively than that of the amines. As with the aromatic amines, the substitution is preferably in the *para* position, or, if that is occupied, in the *ortho*; examples are the reaction of *p*-cresol<sup>958, 959, 960</sup> and  $\beta$ -naphthol.<sup>958, 959, 960</sup> The effect of substituents other than an alkyl group *ortho* to the hydroxyl group has been investigated to only a limited extent; the yield of the thiocyano derivatives is lowered in the case of an alkoxy (guaicol),<sup>538</sup> hydroxyl (pyrocatechol),<sup>1179</sup> or carboxyl group (salicylic acid).<sup>972b</sup> Thiocyanogen does not react with hydroquinone, resorcinol, pyrogallol, or phloroglucinol.<sup>1179</sup> Some phenols that have been thiocyanated are: phenol,<sup>1129, 1929</sup> *o*-cresol,<sup>983</sup> thymol,<sup>983</sup> and  $\alpha$ -naphthol.<sup>958, 959, 960</sup>  $\alpha$ -naphthol is unique in that it gives a disubstituted product; the reaction may be controlled so as to obtain either the mono- or disubstituted product.<sup>974</sup> In keeping with its phenolic character, carbazole is thiocyanated in the 3-position.<sup>1251</sup>

Aromatic thiocyanates prepared by these methods<sup>864, 865c</sup> may be reduced without isolation to the corresponding thiophenols, which may be used in syntheses.<sup>134, 237, 862, 975</sup>

## Miscellaneous Methods

Aromatic thiocyanates<sup>95, 158a, 220, 285, 434, 581, 624, 625, 790, 811, 978, 1064, 1278, 1607, 1708, 1749, 1832, 1935</sup> and selenocyanates<sup>989.5</sup> may be prepared by the diazonium reaction:

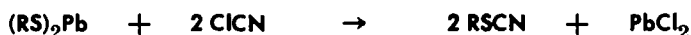


Ferric thiocyanate<sup>320, 1042</sup> and cobalt chloride<sup>194, 434, 1845</sup> have been recommended as catalysts instead of the copper salt. Benzene diazonium thiocyanate is extremely explosive when dry. The *para* chloro derivative is isomerized by hydrochloric acid:<sup>742</sup>

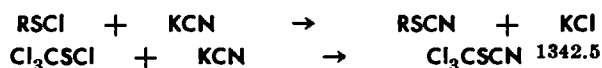


By diazotiazing the following compounds and treating with copper thiocyanate, their corresponding thiocyanato derivatives were prepared: *o*-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>COOH,<sup>1491.5</sup> 2,4-O<sub>2</sub>N(H<sub>2</sub>N)-C<sub>6</sub>H<sub>3</sub>CHO,<sup>1491.6</sup> sulfonylamidoguanidine,<sup>463.5</sup> 3,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-NH<sub>2</sub><sup>905.5</sup> and *p*-PhC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>.<sup>284.5</sup>

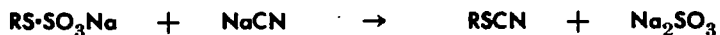
Cyanogen chloride in ether solution reacts with mercaptans<sup>5</sup> or their metal derivatives, preferably lead,<sup>690</sup> to give a thiocyanate: <sup>158a, 1115</sup>



The converse of this is the reaction of a sulfenyl chloride with a cyanide: <sup>1949, 1950, 1951</sup>



Towards KCN, cystine acts as a sulfenyl chloride, giving  $\alpha$ -amino- $\beta$ -thiocyano-propionic acid, NCSCH<sub>2</sub>CH(NH<sub>2</sub>)COOH.<sup>1212, 1601, 1604</sup> An alkyl thiosulfate or RS·SO<sub>3</sub>Na, in which the —SO<sub>3</sub>Na is the negative group, reacts similarly with a metal cyanide:<sup>558</sup>



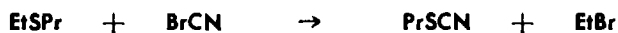
Diazo-methane and -ethane alkylate thiocyanic acid: <sup>1363</sup>



Ethylene oxide reacts with thiocyanic acid to give the hydroxy-ethyl thiocyanate: <sup>1637, 1841b</sup>



Cyanogen bromide splits an alkyl sulfide:



This may be explained by assuming the intermediate formation of the sulfonium bromide,  $\text{EtPrS}(\text{CN})\text{Br}$ ; the alkyl thiocyanate usually contains the heavier group unless this is benzyl.<sup>224, 231</sup>

In the scission of the mixed xylyl sulfides,  $\text{Me}-\text{C}_6\text{H}_4\text{SCH}_2-\text{C}_6\text{H}_4-\text{Me}$ , the  $\text{SCN}$  group goes with the *meta* half rather than with the *para*; and with the *ortho* in preference to either the *meta* or *para*.<sup>231</sup>

A solution of kojic acid in acetic acid treated with potassium thiocyanate and bromine gives the hexathiocyanate.<sup>1912.6</sup>

2-Amino-4-arylthiazoles with ammonium thiocyanate and bromine in acetic acid give 4-aryl-5-thiocyanato-2-aminothiazoles.<sup>1181.5</sup>

N,N-dimethylaminomethylferrocene methiodide refluxed in aqueous potassium thiocyanate yields ferrocenylmethyl thiocyanate.<sup>1315.5</sup>

The elimination of water from a mono-thiocarbamate or of hydrogen sulfide from a dithiocarbamate leaves the thiocyanate:<sup>387</sup>



In the preparation of glycolylecyanamide from sodium ethylate, thiourea, and ethyl glycolate, some glycolyl thiocyanate was obtained as a by-product; lactyl thiocyanate was obtained similarly.<sup>357</sup>

Condensing aliphatic or cycloaliphatic ketones with hydrazine in the presence of alkali-metal thiocyanates give organo-thiocyanato compounds of the probable formula,  $(\text{NHCR}_2\text{SCN})_2$ , where  $\text{CR}_2$  is isopropylidene or cyclohexylidene. They are said to be useful intermediates.<sup>334</sup>

### REACTIONS OF THIOCYANIC ESTERS

It is characteristic of both thiocyanates and isothiocyanates that the radical, whether alkyl or aryl, holds on to the atom to which it is attached. A thiocyanate will nearly always give a product containing  $\text{R}-\text{S}-$  whether it be  $\text{R}-\text{SH}$  or  $\text{R}-\text{SO}_3\text{H}$ ; an isothiocyanate, one having the  $\text{R}-\text{N}=\text{}$  as part of an amine or amine derivative.



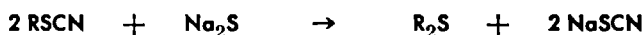
## BREAKING THE R—SCN BOND

As has been mentioned in previous sections and will be taken up more extensively later on, certain alkyl thiocyanates isomerize to the isothiocyanate:



This involves a breaking of the R—SCN bond and occurs only when this is weak. Towards triethylamine, methyl and ethyl thiocyanates act as alkyl halides, forming tetraalkyl ammonium thiocyanates.<sup>1091, 1166</sup> Methyl and benzyl thiocyanates combine with thioureas to form thiuronium salts, as if they were alkyl halides.<sup>1758</sup> Heating a mixture of BuSCN, aqueous  $\text{NH}_4\text{HS}$  containing sulfur, and pyridine at  $175\text{--}80^\circ$  converts the BuSCN into butyramide. Under similar conditions  $\text{PhCH}_2\text{SCN}$  is converted into benzamide.<sup>1591</sup>

In alcoholic solution an alkyl thiocyanate reacts with  $\text{Na}_2\text{S}$  as would an alkyl halide:



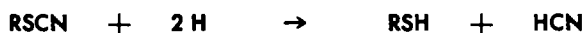
The SCN ion, which is formed quantitatively, can be titrated, giving a method for the analysis of thiocyanates, both aliphatic and aromatic.<sup>497, 1366</sup> The reaction is probably more complicated than is here represented. Instead of alkyl sulfides, disulfides have been obtained along with cyanide ions, indicating that the primarily formed mercaptans had robbed a part of the thiocyanate ions of their sulfur.<sup>256, 286a, 1142a, 1890</sup> Selenomercaptans are prepared by the reduction of organic selenocyanates.<sup>1712</sup> Isotopic exchange takes place between potassium thiocyanate and organic thiocyanates.<sup>1361</sup> In all of these reactions the R—SCN bond is broken and the pseudo-halogen character of the R—SCN group shown.

In orienting influence, the —SCN group is similar to that of the halogens, though somewhat stronger, but weaker than a methyl group. The nitro group enters either *ortho* or *para* in phenyl thiocyanate and *ortho* to the —SCN group in *p*-chloro- and *p*-bromophenyl thiocyanate. In *p*-tolyl thiocyanate, it enters the 2-position for the most part but some of the 3-nitro is formed. The iodine in *p*-iodophenyl thiocyanate is subsituted by the nitro group.<sup>319, 321</sup>

## BREAKING THE RS—CN BOND

*Reduction*

The simplest reaction is: 425, 537, 637, 658d, 728, 813, 814, 991, 1642, 1846



The hydrogen may come from zinc<sup>537</sup> and acid, or from electrolysis with a mercury cathode.<sup>1616</sup> Lithium aluminum hydride<sup>1723, 1724</sup> reduces 1,2-dithiocyanatocyclohexane to 1,2-cyclohexanedithiol.<sup>1272</sup> The reduction of phenacyl thiocyanate with zinc and acid gives phenacyl mercaptan.<sup>466</sup> Thiocyanopyrrole<sup>1431</sup> and ethyl thiocyanate<sup>813, 814</sup> have been reduced by sodium in ethanol.

*Chlorination*

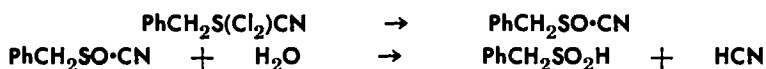
With chlorine, the primary reaction may be assumed to be:



What further reactions take place depend on the conditions. In water below 5°C, methyl thiocyanate gives methanesulfone chloride,  $\text{MeSO}_2\text{Cl}$ , and cyanogen chloride,  $\text{ClCN}$ .<sup>914</sup> Benzyl thiocyanate gives  $\text{PhCH}_2\text{SO}_2\text{Cl}$ <sup>1046, 1286.5</sup> at room temperature, but in ice water the final product is the sulfinic acid,  $\text{PhCH}_2\text{SO}_2\text{H}$ . The primary reaction may be addition of chlorine to sulfur:<sup>828b</sup>



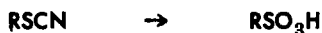
This would be followed by hydrolysis:



With ethyl thiocyanate, chlorination of the ethyl group may take place, giving  $\text{C}_2\text{H}_3\text{Cl}_2\text{SCl}$  and  $(\text{ClCN})_3$ .<sup>899c, 899e, 899h</sup> Chlorination of methyl thiocyanate in sunlight gives carbon tetrachloride, cyanogen chloride, and hexachloromethyl sulfide.<sup>1494</sup>

*Oxidation*

The oxidation of thiocyanates is a convenient method for preparing sulfonic acids:



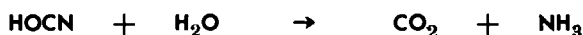
Nitric acid is the usual oxidising agent.<sup>193, 268a, 610, 728, 768, 813, 814, 899a, 899d, 899f, 899g, 991, 1020, 1110, 1220, 1290</sup> The oxidation may be effected by alkaline hypochlorite,<sup>366</sup> sodium hypoiodite,<sup>1903</sup> hydrogen peroxide,<sup>1058, 1394</sup> or electrolytically.<sup>539, 540</sup> There is always the possibility of over-oxidation to sulfuric acid.

### Hydrolysis

The addition of water to a thiocyanate gives different products according to conditions. A simple hydrolysis would be expected to be:



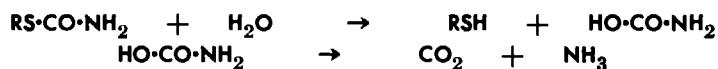
Hydrolysis of the cyanic acid may take place:



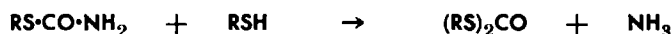
Or it may be assumed that in the hydrolysis of thiocyanates water is taken up by the  $-\text{CN}$  group: <sup>178, 367, 567a, 567b, 567c, 637, 813, 814, 1020, 1027, 1415, 1551, 1588, 1842a</sup>



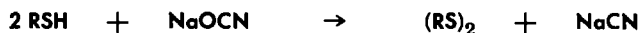
This would be hydrolyzed:



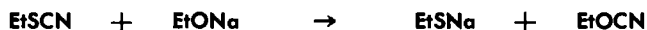
In the presence of sulfuric acid the mercaptan may react with the thiocarbamate: <sup>606c</sup>



In alkaline hydrolysis the mercaptan is oxidised to the disulfide at the expense of a part of the cyanate: <sup>256, 268a, 268b, 286a, 728, 772, 991, 1142a, 1544, 1690, 1890</sup>



By adding sodium picrate solution after the alkaline hydrolysis, a color is developed on which may be based a colorimetric determination of an alkyl thiocyanate.<sup>990</sup> The mercaptan may be oxidised by sulfuric acid<sup>606c</sup> to the disulfide. With sodium ethylate in ethanol the analogous reaction would be: <sup>1524</sup>



In the presence of water there would be hydrolysis and ultimate oxidation of the mercaptan at the expense of the cyanate ion.

Cholesteryl thiocyanate is converted to the disulfide by boiling with sodium methylate.<sup>1280</sup> At 150° C, absolute ethanol saturated with HCl decomposes an alkyl thiocyanate into the mercaptan and cyanuric acid.<sup>1829</sup> This must be hydrolysis, the water coming from the reaction of hydrogen chloride and ethanol.

As the hydrolysis of thiocynoacetic acid produces a weaker acid, the reaction can be followed by measurements of conductivity:



The value of *K* for the hydrolysis is  $1.73 \times 10^{-3}/\text{min.}$ <sup>1882</sup>

With only a little water, the thiocarbamate first formed reacts with unchanged thiocynoacetic acid:<sup>1020</sup>



The reaction of silver nitrate and the sodium salt of thiocynoacetic acid gives  $\text{AgS}\cdot\text{CH}_2\text{CO}_2\text{Ag}$ ; this also involves hydrolysis of the  $\text{—C:N}$  group.<sup>1020</sup>

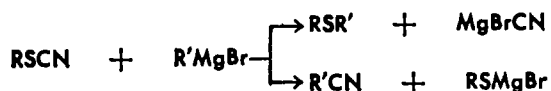
The phenylhydrazine salt of thiocynoacetic acid isomerizes into carbaminethioglycolic phenylhydrazide:



The molecule of water that is given off at one end of the molecule is taken up by the other.<sup>572</sup>

### Other Reactions

The Grignard reagent breaks the bond between the sulfur atom and the cyanogen group. The magnesium can combine with the  $\text{R—S—}$  or the  $\text{=CN}$  group so that the reaction goes in two ways:<sup>8</sup>



When  $\text{R'}$  is aromatic, the second reaction predominates.

The copper salt of acetoacetic ester reacts with ethyl thiocyanate giving cuprous mercaptide, ethyl disulfide, and cyan-acetoacetic ester.<sup>1035</sup>

Ethyl thiocyanate is decomposed by  $\text{PI}_3$  in the presence of

water. The mercaptan and ethyl dithiocarbonate,  $(\text{EtS})_2\text{CO}$ , are among the products.<sup>658a, 658d</sup>

Alkyl thiocyanates react with esters of acids of trivalent phosphorus to form O,O,S-trialkylthiophosphates.<sup>1884</sup>

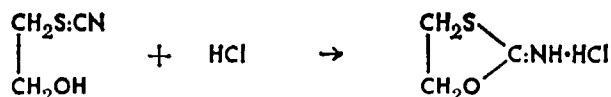
#### ADDITION TO TRIPLE BOND OF $-\text{CN}$ GROUP

The addition of water has been mentioned above. The addition of alcohol to a thiocyanate takes place to form a thioimino ester in the presence of hydrogen chloride.<sup>367, 1027, 1458</sup>



Thiocyanates react with alcohols and olefins in the presence of sulfuric acid to yield N-substituted thiocarbamates. Detailed procedures have been described.<sup>1495.5</sup>

Et-3-nitropyridyl-4-thiocarbamate has been prepared from EtOH and 3-nitro-4-thiocyanatopyridine.<sup>1742</sup>  $\beta$ -Hydroxyethyl thiocyanate gives a cyclic thioiminoester:<sup>1637, 1638</sup>



In the absence of hydrochloric acid it condenses to 1-hydroxyethyl- $\mu$ -mercapto-dihydroimidazole.<sup>1637, 1639</sup>

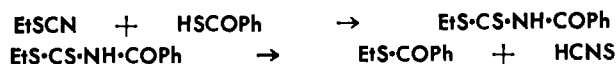
A thiocyano ketone,  $\text{RCOCHR'SCN}$ , can be condensed to a 2-chlorothiazole by treatment with HCl followed by sodium carbonate.<sup>1646</sup>

Toward hydrogen sulfide, an alkyl thiocyanate acts as a nitrile: 193, 222b, 367, 412c, 637, 813, 814, 903a

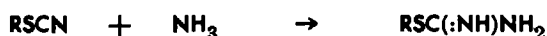


The product is a dithiourethane.

The reaction of a thiol acid with an alkyl thiocyanate serves to distinguish it from an isothiocyanate. There is addition and then the elimination of thiocyanic acid: 812b, 1876, 1877a, 1877b, 1877c, 1878a 1878b,



The addition of ammonia should give the unstable S-alkyl isothiuronium base:



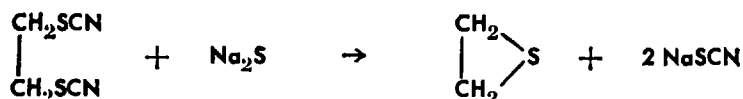
The stable salts of such bases are the well-known addition products of alkyl halides to thiourea (see Chapter 1 of Volume V).

When dry hydrogen iodide or hydrogen bromide is passed into ethyl thiocyanate, crystalline addition compounds,  $\text{EtSCN}\cdot\text{HI}$  and  $\text{EtSCN}\cdot\text{HBr}$ , separate out. These are hydrolyzed by water.<sup>658d, 779f</sup> They appear to be similar to the addition products that nitriles form with these hydrogen halides. They may have the structure  $\text{RSC}(:\text{NH})\text{Cl}$ . In the presence of zinc chloride and hydrogen chloride an alkyl thiocyanate condenses with resorcinol.<sup>984</sup> This may be formulated as the reaction of an acid chloride:



The product is an imidothiol ester hydrochloride or an alkyliso-thiobenzamide salt.

Vicinal<sup>289a, 413, 414a, 414b, 1661</sup> dithiocyanates give cyclic sulfides:



This was the accepted way of preparing such cyclic sulfides until the recent discovery of the reaction of ethylene oxide and potassium thiocyanate:



Ammonium hydroxide produces the disulfide.<sup>1056</sup> The mechanism of this reaction has been investigated;<sup>1661</sup> see Volume III, page 14.

Thiocyanoacetic acid and its esters are condensed to thiazoles by hot concentrated hydrochloric acid.<sup>1020</sup>

Aryl thiocyanates do not undergo the Bayer condensation with chloral in the presence of sulfuric acid, but form compounds of the type  $(\text{ArSCONH})_2\text{CHCCl}_3$ .<sup>899e, 1499</sup>

### Physiology

There have been many investigations of the effects of salts and derivatives of thiocyanic acid on physiological processes.<sup>345</sup>

Potassium thiocyanate is a normal constituent of the blood,

occurring in quantities from 0.0 to 0.6 mg per 100 cc in man.<sup>105, 316</sup> An earlier estimate gave higher figures 0.31 to 2.55 mg/100 cc with 1.3 mg as the average.<sup>1790</sup> The thiocyanate content is higher in smokers.<sup>874, 1608, 1790</sup> Ingestion of thiocyanates may raise this amount to 30 times normal.<sup>1608</sup> The thiocyanate content of the blood of various animals and insects has been determined;<sup>82, 1344</sup> and in the serum of cows it has been found to be 2–3 mg/100 cc of plasma.<sup>1913</sup> The thiocyanate ion is present in milk,<sup>182</sup> in saliva,<sup>332</sup> and in urine,<sup>332</sup> as well as in blood.<sup>121, 1790</sup> In an animal body nitriles have been found to be partially converted to thiocyanate ions,<sup>430, 1374</sup> an excess of which has been found in the blood of dogs exposed to vapors of acrylonitrile.<sup>1087</sup> Considerable hydrocyanic acid is formed during natural putrefaction and it may be converted to thiocyanic acid by sulfur.<sup>1828</sup> By direct reaction with potassium cyanide, L-Cystine, cysteine hydrochloride, sodium cysteinate, and sodium thiosulfate cause the formation of thiocyanate in the living body with resultant detoxication.<sup>1039</sup>

The effect of thiocyanate on the oxygen content of venous blood,<sup>676</sup> the permeability of blood cells to thiocyanate,<sup>1419</sup> and its conversion to cyanide in the blood<sup>677</sup> have been investigated. The lowering of blood pressure by the administration of salts<sup>100, 314, 1216, 1753</sup> and derivatives of thiocyanic acid has been studied extensively. Clinical tests with sodium, potassium, magnesium, and particularly ammonium, thiocyanates have shown definite hypotensive action.<sup>86, 272</sup> A blood level of 4–5 mg % of SCN<sup>-</sup> produces definite hypotension in young or middle-aged people.<sup>1691</sup> The optimum level in blood is 8–12 mg %; a lethal dose is 40 mg.<sup>1</sup> Sodium thiocyanate is less toxic to heart muscles than is the ammonium or potassium compounds.<sup>1691</sup> Injections of vitamins A or K (15–20 × 10<sup>4</sup> units/day) improve the antihypertensive action.<sup>1691</sup> A mixture of acetylcholine and potassium thiocyanate has been recommended.<sup>1518</sup> Thiocyanate compounds lower blood pressure,<sup>294, 408, 1667, 1739</sup> and this effect may last for many months.<sup>1771</sup> The use of thiocyanate compounds in hypertension has been reviewed with 49 references.<sup>1771</sup> Alkothiocyanate derivatives of tetrahydroberberine<sup>1748.5</sup> and *m* and *p* thiocyanobenzoic acids<sup>1051</sup> are reported to have strong action in lowering blood pressure. Intravenous injection of thiocyanate ion increases leucocyte count, increases gastric secretion, slows the

heart, and lowers blood pressure.<sup>1739</sup> Sodium thiocyanate alone has no effect on certain isolated organs but it does increase their response to pilocarpine<sup>1467</sup> and acetylcholine.<sup>1340, 1463, 1464, 1465, 1466</sup>

The effects of administering thiocyanate on the metabolism of iodine in the thyroid gland has been rather extensively investigated.<sup>58b, 114, 131, 623, 845, 1165, 1303, 1364, 1461, 1665, 1703, 1818, 1819, 1897, 1904, 1906</sup> Thiocyanates tend to produce goiter<sup>1028</sup> but only in the absence of added iodine.<sup>58a</sup> They block the formation of the thyroid hormone.<sup>1474</sup> The uptake of labeled sulfur (injected as  $S^{35}CN$ ) by thyroids of rats with low thiocyanate levels<sup>1909</sup> and of hamsters<sup>1145b</sup> has been determined. Change in thyroid caused by occupational exposure to thiocyanates has been observed.<sup>746</sup> A non-toxic salt, erythromycin thiocyanate, is said to be suitable for intramuscular injection.<sup>133</sup> 9- $\alpha$ -Halo-21-thiocyanato-steroids have been prepared and tested for their glucocorticoid activity.<sup>580</sup> It has been found that as many as 40 mols of  $SCN^-$  can be bound to each albumen molecule.<sup>1564</sup> An aqueous solution of thiocyanic acid does not harm the skin.<sup>1930</sup>

Thiocyanates have been found to affect: metabolism,<sup>546, 614, 907, 1218, 1253, 1715, 1798, 1911</sup> the respiration of resting cells of certain bacteria,<sup>1298</sup> skin allergy,<sup>940</sup> liver and kidney functioning,<sup>1217, 1219</sup> heart action in animals<sup>1435</sup> and insects,<sup>1347</sup> and other physiological processes in animals.<sup>104, 379, 803, 830, 1076, 1145a, 1155, 1173, 1348, 1478, 1752b, 1911</sup>

Thiocyanates are antagonistic to lactic acid,<sup>1633</sup> but exert a protective action on ascorbic acid, vitamin C.<sup>730, 1543</sup> They inhibit the catalytic reduction of methylene blue by copper.<sup>1725</sup>

Methyl and 2-hydroxyethyl thiocyanates break dormancy in potato tubers.<sup>718</sup> Growth from dormant plant tissue (tubers, roots, woody plants, grasses, etc.) is delayed 3 to 20 days by benzyl thiocyanate and *o*-chlorobenzyl thiocyanate.<sup>420</sup>

Betaine thiocyanate, m.  $167^\circ$ , has been claimed as a therapeutic agent in promoting the elimination of urea.<sup>142</sup>

Treating *l*-fructose, *d*-glucose, etc. with a solution of thiocyanic acid is said to give compounds of therapeutic value.<sup>943</sup>

### TOXICITY

On account of the extensive use of thiocyanates in insecticides there has been much interest in their toxicity. Small doses of methyl and ethyl thiocyanates cause a primary stimulation fol-



lowed by paralysis of the medullary centers. The toxicity decreases as the carbon chain is lengthened; octyl and decyl thiocyanates are only slightly active, and dodecyl and myristyl even less. Some of the higher homologs cause skin irritation.<sup>1334, 1890</sup> Respiratory stimulation, fall in body temperature, and convulsions are all due to central action; <sup>1511, 1757</sup> certain thiocyanates have a depressant effect on respiration.<sup>757</sup> Aromatic thiocyanates are generally less toxic than aliphatic. The toxicity of dithiocyanates increases with the distance between the groups.<sup>1425</sup> The toxicity of the thiocyanate ion to *Polycellis nigra* is about the same as that of the oxalate.<sup>927</sup> Ferrihemochromogens are an antidote for thiocyanate poisoning.<sup>148</sup>

The toxicological effects of a number of organic thiocyanates have been studied.<sup>302, 1377, 1916, 1924</sup> The toxicities of a number of thiocyanates to goldfish <sup>453</sup> and rats have been determined,<sup>429</sup> and the repellencies of a number of volatile thiocyanates and isothiocyanates have been compared.<sup>135</sup> The toxicities of several thiocyanates to man have been compared with that of DDT.<sup>1102</sup> A review of the literature has been appended to a report of a case of recovery from the thiocyanate poisoning.<sup>403, 1178</sup>

Retention of sulfur occurs to a marked degree after the administration of small doses of ethyl thiocyanate and ethyl and allyl mustard oils to a rabbit.<sup>1555</sup> Octyl thiocyanate does not influence hypotension in a rabbit<sup>10</sup> but it does affect the tonus of the isolated intestine of a guinea pig.<sup>312</sup> The actions of 10 aliphatic thiocyanates on isolated heart of a roach have been compared.<sup>1923</sup> The effects of 2-butoxyethyl-2'-thiocyanoethyl ether on flies and cockroaches have been studied.<sup>370, 755</sup>

#### BACTERICIDAL EFFECTS

The relationship between chemical structure and antibacterial action of aromatic thiocyano-compounds has been investigated.<sup>949, 950</sup> Interesting substituted thiocyanatoanilines and thiocyanatonaphthylamines have been tested.<sup>823</sup> Aryloxyalkyl thiocyanates are claimed to be useful against pathogenic fungi affecting the human skin.<sup>502.5, 833, 1081</sup> Sulfonamides containing a thiocyano group exert a powerful growth-inhibiting action against coccal bacteria.<sup>1746</sup> Mono-, di-, and triethanolamine thiocyanates are said to control growth of bacteria within the mouth.<sup>1025</sup>

Thiocyanic acid,<sup>1827</sup> double thiocyanates of an alkali and hex-

amethylenetetramine,<sup>942</sup> and butyl mercury thiocyanate<sup>996</sup> are said to be useful as disinfectants. Rhodoform, a combination of methyl thiocyanate and hexamethylenetetramine, has been recommended as a urinary antiseptic.<sup>1589</sup> Thiocyanic acid is selectively toxic to tubercle bacilli.<sup>229, 1138, 1955</sup>

Chaulmoogryl, oleyl, and cetyl thiocyanates retard leprosy in mice, but the dithiocyanates from the addition of thiocyanogen to chaulmoogric and hydnocarpic acids are inactive.<sup>49a, 49b, 1841a</sup> Chaulmoogryl choline thiocyanate, m. 76°, has no effect on leprosy mice or on tuberculous guinea pigs, but trimethylchaulmoogryl ammonium thiocyanate is effective.<sup>1833</sup> Morpholine thiocyanate is said to have analgesic properties.<sup>1636</sup>

### Applications

Cation-exchange resins may be prepared by polymerizing vinyl thiocyanate.<sup>854</sup> Resinous condensation products have been obtained from formaldehyde with ammonium thiocyanate<sup>894</sup> and with thiocyano-diamidine.<sup>1053</sup> The addition product of thiocyanogen to partially hydrogenated polybutadiene is thermoplastic.<sup>930</sup> Plastics have been obtained from the condensation of aminocarboxylic or dicarboxylic acids with a thiocyanate.<sup>83</sup> 2-Thiocyanato-4,6-diamino-s-triazine has been used as an intermediate in the preparation of synthetic resins and dyes.<sup>1573</sup>

The addition products of certain thiocyanates to vinyl aromatic compounds are said to counteract the adverse effect of acetylinic impurities, that interfere with polymerization.<sup>1565</sup> The polymerization of methyl methacrylate or compounds containing C:C bonds is said to be facilitated by calcium<sup>734</sup> or ammonium thiocyanate.<sup>784</sup> Thiocyanates aid in the condensation of diamines with dibasic acids.<sup>84</sup> 2-Thiocyanato-ethylphenylcarbanilates are claimed to be plasticizers for vinyl polymers.<sup>1274</sup> A method has been proposed for obtaining stable polydiene polymers by use of thiocyanates and isothiocyanates.<sup>682</sup> Alkyl primary and secondary amine salts of thiocyanic acid<sup>1205</sup> and 2-thiocyanothiazoline<sup>1204</sup> are claimed as accelerator activators in the vulcanization of natural and synthetic rubbers. 2,6-Bis(thiocyanomethyl)-4-methylphenol, m. 133°, aids the vulcanization of rubber.<sup>1222</sup> An insoluble polymeric film is formed by heating a solution of ammonium thiocyanate in furfuryl alcohol.<sup>1516</sup>

Solutions of chlorinated hydrocarbons are said to be stabilized by methyl and ethyl thiocyanates,<sup>1441</sup> and solutions of pyrethrins and rotenone by a phenoxythiocyanate.<sup>450</sup>

Ammonium,<sup>297</sup> sodium,<sup>297</sup> alkyl,<sup>311, 875, 1530, 1539, 1714</sup> benzyl,<sup>1530, 1625</sup> and aralkyl<sup>311, 875, 1530, 1539, 1625, 1714</sup> thiocyanates, and the condensation product of an aldehyde and a thiocyanate of a tertiary amine<sup>798b, 800</sup> have been recommended as inhibitors of pickling. Nickel and cobalt thiocyanates are said to be suitable for plating these metals on iron.<sup>951</sup>

Quaternary ammonium thiocyanates,<sup>1412</sup> organo-silicon thiocyanates,<sup>934</sup> and compounds of the type,  $\text{RCONHCH}_2\text{SCN}$ ,<sup>1413</sup> are claimed as water repellants for fibers. This subject has been reviewed.<sup>513, 1613</sup> Certain thiocyanates are used to improve the spinning and fibrous properties of polyacrylonitrile polymers.<sup>384, 1587</sup>

Organic thiocyanates,<sup>561</sup> particularly lauryl<sup>461</sup> and nitroaryl,<sup>451</sup> and dodecene dithiocyanate,<sup>1136</sup> are said to be useful in extreme-pressure lubricants. The reaction products of phosphorus pentasulfide with certain alkyl thiocyanates are claimed to improve the oxidation and corrosion-resistant properties of lubricating oils.<sup>1351</sup> Methyl thiocyanate has been proposed as a refining agent for lubricating oils<sup>205a</sup> and for rosin.

Dyes are obtained by coupling diazotized aromatic amines containing thiocyano groups.<sup>727, 856, 858, 859, 866</sup> Salts of  $\text{HSCN}$  are claimed as assistants in dyeing fibers composed of cellulose esters or ethers.<sup>387, 1326</sup>

Octadecyl thiocyanate is a promoter for drop-wise condensation of steam.<sup>177, 180</sup> 2-Thiocyanato-4,6-diamino-s-triazine has been recommended as a mothproofing agent and antioxidant.<sup>939</sup> A thiocyanate complex has been claimed as useful for blasting fuses and caps.<sup>1443</sup>

Thiocyanates have been proposed for a number of uses: to increase the resistance of wool to heat;<sup>101</sup> as antifouling agents;<sup>751</sup> coloring agents for glass;<sup>1160</sup> selective protective action in the flotation of pyrites and arsenopyrites;<sup>1416</sup> and as wood preservatives.<sup>1054, 1610</sup> It is claimed that formation of reddish colors in thiocyanates can be prevented by the addition of small amounts of inhibitors. These include certain salts of dicarboxylic acids.<sup>799</sup>

## THIOCYANATES AND ISOTHIOCYANATES AS PESTICIDES

In recent years there has been much interest in thiocyanates as insecticides, with or without pyrethrum, or mixed with other constituents. Many bulletins,<sup>279, 1287, 1505, 1506</sup> patents, and numerous articles describe their use and effectiveness against various pests. The active agents are usually dissolved in some solvent such as deodorized kerosene and applied as sprays. The normal thiocyanates, RSCN, are preferred to the iso-, RNCS, because they are more effective and their odors are less disagreeable,<sup>248, 251, 254, 259b, 261a, 445, 690, 691, 693, 716, 722, 763, 911, 988, 1139, 1167b, 1170, 1171b, 1191, 1289, 1310, 1319, 1408, 1442, 1554, 1568a, 1624, 1770, 1841c, 1849a, 1898, 1899</sup>

A relation between knock-down activity for flies and chemical constitution of some thiocyanates has been proposed<sup>705, 1198</sup> as well as a mechanism of action.<sup>872</sup> A mixture of octyl and decyl thiocyanates is active in fly sprays;<sup>212, 213, 756b, 1493</sup> dodecyl is particularly effective also against a number of pests<sup>721, 839, 901, 989, 1066, 1236, 1476, 1650</sup> and their eggs,<sup>140</sup> but not all.<sup>528, 840, 931</sup> The higher members of this series—myristyl,<sup>721</sup> cetyl,<sup>552, 989</sup> stearyl<sup>552</sup>—are less potent. Various thiocyanates have been tested against mosquitoes, mostly as repellants.<sup>135, 421, 1488, 1492, 1675, 1738, 1791, 1823, 1856</sup> Methyl and ethyl thiocyanates are reported to be extremely toxic to red scale in citrus fruit.<sup>390</sup> Thiocyanates have also been tested as a component of preparations for control of the Mexican bean beetle,<sup>44</sup> fruit-tree red spider,<sup>482</sup> mealy bugs,<sup>1311</sup> cabbage caterpillar,<sup>1482</sup> and *myzodes persicae* on tobacco plants.<sup>1563</sup> The effect of thiocyanate sprays on the pectic content of apples has been studied.<sup>464</sup> Butyl thiocyanate is potent against tobacco moth but does not harm the moth eggs.<sup>1762</sup> 2-Butoxy-2'-thiocyanoethyl ether is particularly good against bed bugs;  $\alpha$ -naphthyl and lauryl thiocyanates also are effective.<sup>290</sup> Butyl carbetyl and lauryl thiocyanates have been studied as stomach poisons.<sup>1199</sup> Alkyl (isothiocyanomethyl) benzoates are claimed as having good insecticidal activity both in the stomach and in contact against scaly and soft-bodied insects.<sup>499</sup> Compounds containing an alkylene group have also been claimed as insecticides.<sup>334.5</sup> Organic thiocyanates having the general formula  $X_3CRSCN$  and  $X_2C:CHRSCN$ , (where R is an alkylene radical and X chlorine or fluorine), are reported to be useful as contact

insecticides, and as plasticizers for resins.<sup>1552b</sup> Phenyl thiocyanate is more effective against insects than aliphatic compounds.<sup>1058</sup> Lauryl thiocyanate<sup>1146</sup> is much less toxic than butylcarbityl,  $\text{BuOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SCN}$ ,<sup>293</sup> which is not a health hazard when properly used as an insecticide.<sup>1288b</sup> Claimed as insecticides are also naphthyl,<sup>1552a</sup> terpene,<sup>201b, 876, 1773</sup> and bornyl<sup>1552a</sup> thiocyanates, those from hydrogenated isophorones,<sup>260b</sup> thiocyanated phosphite esters,<sup>381b</sup> esters of thiocyano-fatty acids,<sup>207, 1705, 1896.5</sup> cyclohexylcarbinythiocyano esters,<sup>1267</sup> allyl isothiocyanoethers,<sup>499.5</sup> allyl mustard oil<sup>1168, 1765</sup> and certain aromatic isothiocyanates.<sup>674, 789, 1471</sup>

There has been a great deal of interest in thiocyanates, the aliphatic chains of which contain one or more ether linkages or other "negative" groups. One of these, 2-butoxy-2'-thiocyanoethyl ether,  $\text{BuOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SCN}$ —sometimes called butylcarbityl thiocyanate—<sup>119, 290, 383, 479, 756a, 792, 1182, 1288a, 1312, 1417, 1429, 1476, 1650, 1802, 1912</sup> has attained commercial importance as a constituent of one variety of "Lethane." 2-Thiocyanoethyl laurate goes along with it. Numerous articles and patents<sup>380, 770, 789a, 1288c, 1512</sup> have been written on varieties of "Lethane,"<sup>217, 247, 365, 553, 593, 910, 1059, 1099, 1146, 1167a, 1211, 1396, 1500, 1620, 1706, 1754, 1849b, 1855</sup> The "Lethanes" are said to be effective in controlling the leafhopper,<sup>1810</sup> potato insects,<sup>723</sup> and onion thrips,<sup>199</sup> and are only slightly repellant to termites.<sup>838</sup>

Aryl thiocyanates, such as phenyl,<sup>1674, 1886</sup> benzyl,<sup>249, 821, 1870</sup> naphthyl,<sup>1355, 1784, 1785</sup> naphthylmethyl,<sup>1509</sup> and others,<sup>499, 1573</sup> which are effective insecticides, are said to be rendered more potent by certain substituents in the aromatic nucleus,<sup>279, 790, 869, 1733, 1756</sup> and by introducing a second  $-\text{SCN}$  group.<sup>856, 858, 859, 867, 1567, 1568d, 1870</sup> The thiocyano group may be at the end of a chain joined directly<sup>264, 759</sup> to the nucleus, as in  $\text{ArCH}_2\text{CH}_2\text{CH}_2\text{SCN}$ , or by an ether linkage, as in  $\text{ArOCH}_2\text{CH}_2\text{SCN}$ ,<sup>361, 362, 363a, 363b, 363c, 381a, 771, 1133, 1134</sup> 2-Thiocyanoethyl piperate is only moderately effective.<sup>1735</sup>

Esters of thiocyanoacetic acid have become commercially important as constituents of "Thanite." They can be made by adding the thiocyanoacid to an unsaturate,<sup>202</sup> but the usual method is to add a halogenated acid, such as chloracetic, to an unsaturated hydrocarbon, commonly a terpene, and then cause this ester to react with a soluble salt of thiocyanic acid. These esters,

either dissolved in oil or in water emulsion, are used in sprays against flies and other insect pests.<sup>59, 60, 1099, 1408, 1492, 1647, 1648, 1694, 1754, 1855</sup> In a series, the efficiency as an insecticide increases with the molecular weight of the alcohol and decreases with that of the acid.<sup>1231</sup> 2-Butoxy-2-thiocyanodiethyl ether, 2-thiocyano esters of certain higher fatty acids, bornyl, and isobornyl thiocyanates have been tested in mixtures for the formation of insecticide films on building materials.<sup>791</sup>

Allyl mustard oil in a concentration of 0.12 mg/liter,<sup>1557</sup> (or 0.07 if the time is prolonged,<sup>1755</sup>) kills house flies, repels certain other flies,<sup>1371</sup> and kills the larvae of Japanese beetles,<sup>551</sup> of May beetles,<sup>1765</sup> and of the codling moth.<sup>1171a</sup> Ethyl isothiocyanate is fairly effective against larvae of the codling moth.<sup>1163</sup>

A certain surface-active compound has a thiocyanate group at one end of a carbon chain and a quaternary ammonium group at the other.<sup>630, 1279</sup> In tests on flies,<sup>1438</sup> phenyl isothiocyanate has a substantially lower LD<sub>50</sub> value than does DDT.

Of the aliphatic dithiocyanates so far tested, the trimethylene appears to be the best<sup>756b, 1341, 1473, 1885</sup> and it is also equivalent to Bordeaux mixture and sulfur dust against leaf mold.<sup>1886</sup> A number of dithiocyanates having hetero atoms in the chains have been claimed; among these is one from mustard gas,  $S(CH_2CH_2SCN)_2$ .<sup>825, 826, 1512, 1870</sup> The corresponding oxygen compound,  $O(CH_2CH_2SCN)_2$  has shown promising results<sup>51, 458, 1541</sup> and does not seem to hinder germination of pollen.<sup>51</sup> The dithiocyanate<sup>211</sup> made by adding thiocyanogen to diisobutylene has been claimed as an insecticide. 1,2-Dibromo-1,2-dithiocyanethane,<sup>1259</sup> dinitrophenylthiocyanate,<sup>185</sup> and thiocyananiline<sup>343</sup> have been tested as seed disinfectants. It is said that dithiocyanates having both  $-SCN$  groups on the same carbon atom are more active than those in which they are separated.<sup>1567</sup>

The odor of thiocyanate and isothiocyanate insecticides is claimed to be improved by the addition of urea or thiourea<sup>304</sup> or by solvent extraction, which removes the odorous materials.<sup>201a</sup> In killing power for body lice, 2-butoxy-2'-thiocyanoethyl ether stood highest; decyl and dodecyl came next, and myristyl, cetyl, and octadecyl were progressively poorer.<sup>281, 631</sup> 2-Butoxy-2'-thiocyanoethyl ether has been tested as an ovicide.<sup>426</sup> Butyl carbityl thiocyanate mixed with  $\beta$ -thiocyanoethyl laurate is recommended against lice.<sup>516</sup> Tests have been conducted against body lice,<sup>483</sup>

and their eggs;<sup>484</sup> and a comparison has been made of thiocyanates with other insecticides against the louse and the bed-bug.<sup>281</sup> Thiocyanates have shown effectiveness in the control of lice on animals.<sup>19, 382, 794, 1210, 1652</sup> Rotenone and bis-(thiocyanoethyl)ether gave poor control of cabbage pests,<sup>692</sup> although the addition of rotenone to other insecticides was reported to give good control of leaf hoppers and aphids.<sup>1286</sup> Methyl thiocyanate, also an effective ovicide for lice,<sup>1884</sup> is quite toxic to both eggs and larvae of *Dacus dorsalis*. Ethyl thiocyanate is more toxic to the eggs than to the larvae.<sup>91</sup>

Lauryl thiocyanate,  $\beta$ -butoxy- $\beta'$ -thiocyanoethyl ether,<sup>1255</sup> and phenylethyl thiocyanate<sup>833</sup> have been compared with other fungicides. Esters of thiocyanoacetic acid,<sup>598, 833, 1266, 1630, 1800</sup> and phenyl thiocyanate<sup>598</sup> and some of its substituted derivatives are effective for inhibiting growth of mold in foodstuffs.<sup>597, 598, 599</sup> The 2,4-dinitrophenyl thiocyanates have been found to be active as fungicides and for prevention of mildew.<sup>395, 503, 1117</sup> Certain diisothiocyanates are said to be potent against fungi,<sup>341, 525</sup> the activity of the alkylene type decreasing with the length of the chain. The diiso- are more effective than the monoisothiocyanates.<sup>1023.5</sup> Thiol compounds almost nullify the fungitoxicity of tetramethylene diisothiocyanate.<sup>1663</sup>

Trithiochloromethyl<sup>1342, 1342.5</sup> and other thiocyanates<sup>520, 1736</sup> are said to be effective against root-knot nematode, peach-rot fungus, apple bitter-rot fungus, and many bacteria. *trans*-Dithiocyanoethylene<sup>1324</sup> thiocyanonicotines,<sup>1861</sup> ethylene-,<sup>992</sup> butylene-,<sup>992</sup> hexylene-,<sup>992</sup> and octylene-<sup>992</sup> diisothiocyanates, 3,4-methylhydroxyphenylisothiocyanate,<sup>14</sup> 3,4-chlorohydroxyphenylisothiocyanate,<sup>14</sup> allyl mustard oil<sup>1376, 1449, 1852, 1853</sup> and phenethyl isothiocyanate<sup>832</sup> have been reported as fungicides. The fungicidal activity of aromatic thiocyano compounds against phytopathogenic microorganisms has been compared.<sup>947, 948</sup>

The more volatile alkyl thiocyanates and isothiocyanates have been of interest as fumigants.<sup>760b</sup> To protect a thousand cubic feet of grain against weevils requires 0.2–0.3 lb of methyl compared to 2–2.5 lb of ethyl thiocyanate and 0.9 lb of allyl mustard oil.<sup>760a, 1309</sup> The methyl compound approaches hydrocyanic acid in effectiveness.<sup>549, 1653</sup>

Slow-burning mixtures of heavy metal thiocyanates and oxidising agents have been claimed for the vaporization of insecti-

cides.<sup>1456</sup> On a molecular basis, methyl thiocyanate is as toxic as hydrocyanic acid but it is injurious to citrus trees.<sup>1084</sup> The addition of an irritant such as allyl mustard oil to hydrocyanic acid is said to increase the kill by stimulating respiration.<sup>1318</sup> Ethyl and methyl thiocyanates do shorten the time for killing by hydrocyanic acid.<sup>1434</sup> Allyl isothiocyanate is effective against wire worms<sup>1100</sup> and has been recommended for use in spraying trees,<sup>827</sup> as has phenyl isothiocyanate in an oil emulsion.<sup>697</sup>

Various thiocyanates have been found to protect plants from insects but they caused damage to the plants.<sup>693, 1167b</sup> It has been suggested that mustard oil lowers the resistance of plants to disease.<sup>832</sup> Various organic thiocyanates have been claimed as herbicides.<sup>218</sup> Allyl mustard oil decreases the emergence of eel worm larvae and so protects potato roots;<sup>495</sup> and it is also reported to be effective against fruit fly larvae.<sup>804</sup>

Allyl mustard oil is a repellent for certain kinds of flies<sup>1074</sup> and is a soil pesticide.<sup>333</sup>

2,4-Dinitrophenyl,<sup>346</sup> 4-*t*-butylcyclohexyl,<sup>1896</sup> nitroaromatic,<sup>554, 855</sup> alkyl ammonium thiocyanates,<sup>1711.5</sup> and others of this type<sup>554, 855</sup> have been considered as pesticides. Propyl- and isopropyl mercuric thiocyanates have been tested as molluscicidal agents.<sup>197</sup>

A comparison has been made of the harmfulness to plants of thiocyanates with other insecticides.<sup>1099</sup> Objections have been made to the use of some organic thiocyanates.<sup>1430</sup> The toxicity of flue dusts containing various amounts of thiocyanates has been determined.<sup>467</sup>

## Isothiocyanates

### OCCURRENCE AND HISTORY

The normal esters RSCN are extremely rare, if indeed they are ever found in natural products; but it is quite different with the isothiocyanates. A survey has been made of naturally occurring isothiocyanates,<sup>1007</sup> a number of which are found in the volatile oils from plants. The only one of importance is the allyl compound, the chief constituent of oil of mustard.<sup>411, 761, 1295, 1872</sup> This and other isothiocyanates are present as glucosides in the seeds of various plants<sup>1011, 1012, 1013, 1013.8</sup> All isothiocyanic esters, aryl and alkenyl as well as alkyl, are called *mustard oils*. The study of allyl isothiocyanate engaged the attention of a number of organic chemists during the second quarter of the nineteenth



century.<sup>54, 151, 215a, 215b, 216, 280, 305, 459, 531, 556, 656, 711, 780a, 842, 1142b, 1143, 1152, 1333, 1508, 1586, 1594, 1666b, 1768, 1869, 1892a, 1893a, 1893b, 1954</sup> and working out the structure of mustard oil was an important item in the development of ideas of valence, structure, and isomerism. It was all the more interesting because nitrogen and sulfur were involved, in addition to carbon and hydrogen.

By macerating black mustard seed with ethanol, filtering, and evaporating the solution, a crystalline substance is obtained; but by grinding the seed with water, keeping the mixture warm for several hours and steam-distilling, an oil is isolated.<sup>556</sup> Contact with warm water for a time is necessary for the liberation of the oil.<sup>215a, 215b, 305, 459, 531, 711, 780a, 1142b, 1143, 1666b</sup> If the mustard seed meal is treated with ethanol at 40° and then with water, no oil can be obtained.<sup>215a, 215b</sup> If the crystalline substance obtained with ethanol, is treated with a cold water extract of the meal, the oil is liberated.<sup>1152</sup> The oil is not present in the mustard seed in the free state.<sup>216, 556, 656, 711</sup>

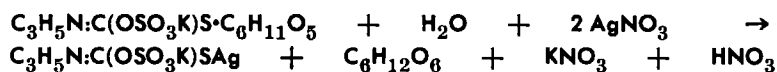
The seed contain two substances,<sup>280</sup> potassium myronate (also called *sinigrin*), the glucoside (sinapin<sup>216, 531, 780a</sup> and sinapisin<sup>1666b</sup> in old literature) which yields the oil on hydrolysis, and myrosine which brings about that hydrolysis.<sup>1586</sup> The myrosine is soluble in water but insoluble in ethanol. It is inactivated by heating to 70° C or by ethanol at 40° C. The two substances are stored in different parts of the seed. The rupture of the cell walls permits them to come together and, if water is present, hydrolysis takes place. This may be brought about by chemical means.

Sinigrin is a glucoside which is hydrolyzed to glucose, mustard oil, and acid potassium sulfate: <sup>1594, 1893a, 1893b</sup>



The formula has been written  $\text{C}_{10}\text{H}_{18}\text{NS}_2\text{KO}_{10}$  but is properly  $\text{C}_{10}\text{H}_{16}\text{NS}_2\text{KO}_9 \cdot \text{H}_2\text{O}$ .<sup>615a</sup> After drying it melts at 126–7° and shows the rotation  $[\alpha]_D -15^\circ$  at 13° C.

Silver nitrate reacts with sinigrin: <sup>54, 615a, 1593, 1596</sup>



In this cleavage a Walden inversion takes place.<sup>1593</sup> Instead of glucose, a thioglucose may be obtained.<sup>1915</sup>

The oil from black mustard was analyzed by Dumas and

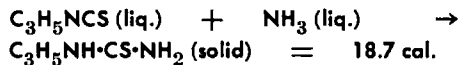
Pelouze<sup>459</sup> in 1833 and found to contain 20.25% of sulfur, 14.45 of nitrogen, 5.02 of hydrogen, 49.98 of carbon, and 10.30 of oxygen. (The correct figures are 32.33, 14.13, 5.08, 48.45 and 0.00.) Their sulfur was far too low and the oxygen was by difference. They determined the vapor density and arrived at the clumsy formula,  $C_{16}H_{10}N_2S_{5/4}O_{5/4}$ . They found that the oil reacted with ammonia to form a crystalline compound containing 42.75% carbon, 6.90 of hydrogen, 24.62 of nitrogen, 16.84 of sulfur, and 8.89 of oxygen, which led to the formula  $C_{32}H_{32}N_8O_{5/2}S_{5/2}$ . The correct percentages are: carbon 41.35, hydrogen 6.94, nitrogen 24.12, sulfur 27.59 and oxygen 0.0. Here again their sulfur was low, illustrating the difficulties under which the early chemists labored. The method of determining sulfur was evidently poor and gave low results. Adding the oxygen, which they reported, to the sulfur gives nearly the correct values for sulfur. A correct analysis of the mustard oil was made by Löwig in 1839.<sup>1142b</sup>

Allyl isothiocyanate becomes discolored on keeping and deposits a dark colored material.<sup>1068</sup> This is more rapid in sunlight.<sup>620</sup> Butyl<sup>1180</sup> and ethyl<sup>1063, 1180</sup> acetates and formic acid<sup>1063, 1180</sup> are said to stabilize the mustard oil.

The reaction of mustard oil with ammonia is: <sup>1143, 1869</sup>



The compound—a thiourea—is known as *thiosinamine*, so named by Varrentrop and Will (thiosinammin,<sup>1892a</sup> thiosinamine).<sup>151</sup> As it is readily formed, easily isolated, and characterized,<sup>1333</sup> it has been of great service in identifying allyl isothiocyanate in oils from various sources.<sup>181, 1666b</sup> The heat of formation of thiosinamine has been measured: <sup>150a</sup>



With 1 part of ethanol and 3 parts of ammonium hydroxide the conversion is complete.<sup>555, 557</sup> The same reaction goes with the chloro-derivative: <sup>779c</sup>



Analogous thiourea derivatives have been relied upon for the characterization of other mustard oils.<sup>842</sup>

Allyl isothiocyanate was prepared from allyl iodide and potassium thiocyanate and shown to have all of the characteristics of the natural oil.<sup>1954</sup>

Allyl isothiocyanate and some free thiocyanic acid are found in onion juice.<sup>1040</sup>

The resemblance of oil of cochlearia to that of mustard was noted. As with mustard, no oil can be extracted from the dry material, but if this is mixed with ground white mustard and water and then steam-distilled, the oil is obtained, boiling some 16° higher than the oil of mustard.<sup>1666a</sup> Analyses of the oil and of its compound with ammonia, m. 135°, <sup>813, 814</sup> showed these to have the composition  $C_4H_9NCS$  and  $C_4H_9NH\cdot CS\cdot NH_2$ . The oil from horseradish <sup>842, 1578.5, 1718</sup> was found to have the same properties and to give the same thiourea derivative. The mustard oil from isobutylamine was prepared. Its boiling point was near enough to that of the natural oil, and the isobutylthiourea from it had the right composition but it melted at 90°. <sup>813, 814</sup> Finally *s*-butyl isothiocyanate was made and found to be identical with the natural product. <sup>813, 814</sup>

This mustard oil is identified by its optical rotation and the properties of the *s*-butylthiourea derived from it,  $[\alpha]_{20/D}$ , 22.77°; m. p., 136–7°. The amount of it present is determined by the rotation and by titration with silver nitrate. <sup>615b, 615c, 615d, 615f, 1276</sup> Of *cochlearia officinalis*, 100 g of blossoms gave 62 mg of the mustard oil; 100 g of the leaves, 9 mg. <sup>181</sup> Oil of scurvy grass contains 94% of this isothiocyanate. <sup>1437</sup> The same mustard oil is found in oil of *cardamine amara*. <sup>532, 1067b</sup> The amount present in horseradish is 128 mg %, in green cabbage, 3.6. <sup>1612</sup> Various mustard oils are found in a variety of plants. <sup>210, 1202, 1576</sup> They are usually present as glucosides which are hydrolyzed by enzymes present in cells of the plants. To test for the presence of a mustard oil in the seeds or leaves of a plant, some of the material is ground up with water and the solution mixed with beer. If such an oil is present, mycoderma is prevented. <sup>1763</sup> The peelings of white turnips contain a glucoside from which phenylethyl mustard oil is liberated. <sup>1067b</sup>

Chromatography has been found useful in isolating the mustard oils from a number of glucosides. <sup>906, 1009, 1010, 1013.5, 1014</sup>

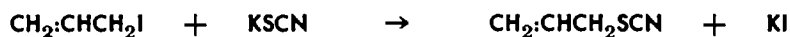
Crotonyl isothiocyanate has been identified in several mustard oils by its boiling point, 175–6° C, and the melting point of its

thiourea derivative, 64°. <sup>33a, 33b, 127a, 1572, 1670</sup>  $\beta$ -Methylallyl isothiocyanate has been obtained from the seed of *conringia orientalis*. <sup>834</sup>

A glucoside was isolated from the seeds of the gold lac, *Cheiranthus cheiri*. <sup>1840</sup> The mustard oil from this was named *cheirolin*. After a long investigation in the course of which a number of synthetic compounds were compared to the natural product, this was shown to be  $\text{CH}_3\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NCS}$ ; and the glucoside,  $\text{CH}_3\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}:\text{C}(\text{SC}_6\text{H}_{11}\text{O}_5)\text{OSO}_3\text{K}$ ,  $[\alpha]_{\text{D}}^{27} 21.09^\circ$ . <sup>1592, 1597, 1598, 1599</sup> In the seeds of *Erysimum perowskianum*, 0–.05% of erysolin, another mustard oil, was found. This was proved to be  $\text{CH}_3\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NCS}$ . <sup>1597</sup> It is very rare that a natural product contains a sulfone group. The oil from *Tropaeolum* seeds has been found to be benzyl mustard oil,  $\text{PhCH}_2\text{NCS}$ ,  $b_{12} 124-5^\circ \text{C}$ . <sup>1595</sup> It is also found in the land cress plant <sup>1169</sup> and in the seeds of other plants. <sup>512.4, 1073</sup> *p*-Hydroxybenzylisothiocyanate is present in the enzymatic hydrolysate of the glucoside of *Sinapis alba*. <sup>31, 1016</sup> Ptergospermine, the antibiotic from the Indian drumstick tree, readily liberates benzylisothiocyanate. <sup>406a</sup> *p*- and *m*-Methoxybenzylisothiocyanates occur as glucosides in *Aubrietia* species and *Limnanthes douglasii*, respectively. <sup>512.5, 1012.5</sup> Phenyl, isopropyl, and *s*-butyl mustard oils are obtainable from glucosides present in seed kernels of *Putranjiva roxburghii*. <sup>1454</sup> 4-Methylthiobutylisothiocyanate is present in seeds of *Eruca sativa*. <sup>1011</sup> Crotonylsenevol, angelylsenevol, and phenylethylsenevol have been isolated from colza seed and rape-seed. <sup>32</sup>

### PREPARATION

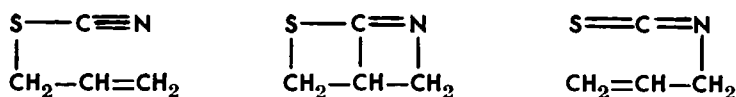
The isomerization into isothiocyanates has been mentioned in a previous section as taking place readily with certain alkyl thiocyanates. This offers a simple method of preparation for the alkyl isothiocyanates that can be formed in this way. From potassium thiocyanate and allyl iodide, an extremely reactive halide, allyl thiocyanate is obtained in a short time even at 0°:



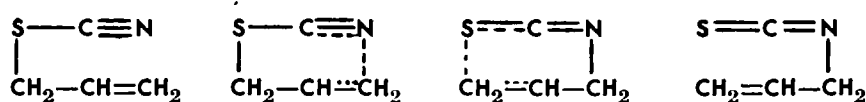
This allyl thiocyanate isomerizes to the isothiocyanate on warming to room temperature. <sup>151</sup> This involves the breaking of the bond between the allyl and the SCN, a pseudo-halogen, which

bond is almost as labile as it is in allyl iodide. When allyl bromide is used in this preparation, the product is allyl isothiocyanate,<sup>228, 637</sup> the isomerization having kept pace with the formation of the thiocyanate. The possibility of isolating a particular thiocyanate depends on the relative rates of its formation and isomerization.

The isomerizing of allyl thiocyanates involves a shift of the sulfur to the gamma carbon atom. This has been explained by assuming a cyclic intermediate:<sup>158b</sup>

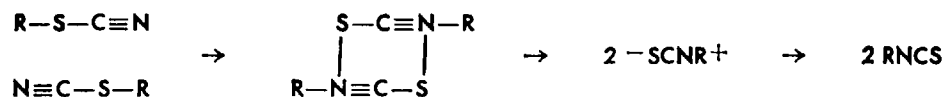


This shift has been shown to take place in the case of crotyl thiocyanate, but not in that of cinnamyl.<sup>158b</sup> A partial valence may become a real bond:



The terminal atoms come close together and their mutual attraction becomes stronger but the bond of the sulfur to the alkyl weakens.<sup>143</sup>

In a previous section it has been stated that the alkyl thiocyanates may serve as alkylating agents. If mutual alkylation should take place between two molecules of an alkyl thiocyanate, the product would be a double-ended salt which might dissociate:



With cinnamyl bromide,<sup>143, 1842a, 1842b</sup> crotyl bromide,<sup>325, 1285</sup>  $\beta$ -chlorocrotonyl bromide,<sup>1399</sup> and chloroacetone,<sup>741a, 1759, 1760, 1761</sup> the thiocyanates have been isolated. With other halides, such as  $\alpha$ -ethyl- $\beta$ -propylallyl chloride,<sup>230</sup> methallyl chloride,  $\text{CH}_2\text{:}-\text{CMeCH}_2\text{Cl}$ ,<sup>263</sup>  $\alpha$ -chlorallyl chloride,<sup>779b, 779d</sup> cyclopentenyl chloride,<sup>227</sup>  $\text{Me}_2\text{CBrCH=CH}_2$ ,<sup>1729</sup> allyl chloride,<sup>856, 860</sup> butadienyl chloride,<sup>301</sup> propargyl bromide,<sup>779c</sup> chloromethyl ether,<sup>915, 1582</sup> dichloromethyl ether,<sup>783</sup> 2-thenyl bromide,<sup>225</sup> allyl-*p*-toluene sulfonate<sup>1510</sup> and allyl potassium sulfate,<sup>1788</sup> only the isothiocyanates have been isolated. Some propenyl isothiocyanate has been found in natural as well as in synthetic allyl isothiocyanate.<sup>1440</sup>

Of the thiocyanates that contain saturated alkyls, the methyl is the only one whose isomerization is practicable. It is largely transformed to the isothiocyanate when it is heated for several hours at 180°. There is also polymerization: <sup>647a, 813, 814</sup>



The presence of salts, particularly cadmium iodide, facilitates isomerization, whereas sulfuric acid promotes polymerization.<sup>647c</sup> There is little isomerization with ethyl thiocyanate and apparently none at all when the alkyls are longer.<sup>1842a</sup> The heat of isomerization is 10.5 Cal. for the methyl and 9.6 for the ethyl compound.<sup>150a, 150b, 150c</sup>

Tetraacetyl-1-thiocyano-β-glucose is isomerized to the isothiocyano on heating to 141° C.<sup>1889</sup>

From ammonium or potassium thiocyanates and acid chlorides, aliphatic and aromatic isothiocyanates are obtained:

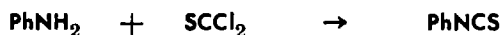


Ethyl chloroformate <sup>710</sup> serves as an acid chloride.<sup>416a, 438, 439, 441a, 441e, 443a, 779e</sup> No evidence has ever been found for the intermediate formation of a thiocyanate.<sup>1874</sup> A solution of the acid chloride in benzene or toluene may be shaken with lead <sup>438, 439, 440, 443a, 1244a, 1244b</sup> or ammonium <sup>438, 449, 1803</sup> thiocyanates. The hydrocarbon solution so obtained may be used for the preparation of derivatives such as thioureas from amines.<sup>443a, 1803</sup> Aromatic acid chlorides react satisfactorily with sodium or ammonium thiocyanates in acetone.<sup>62, 448, 564</sup>

### *From Amines*

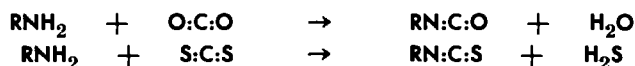
Isothiocyanates are derivatives of amines, and in Beilstein they are to be found under the amines. Most of the isothiocyanates that are not obtainable from thiocyanates by isomerization are prepared directly or indirectly from amines.

As phenyl isocyanate, PhNCO, reacts readily with H<sub>2</sub>O, alcohols, or amines, it is made from aniline hydrochloride and phosgene under strictly anhydrous conditions. Isothiocyanates, either aliphatic <sup>241</sup> or aromatic,<sup>1780</sup> are prepared readily from the primary amines and thiophosgene:



As thiophosgene and isothiocyanates are indifferent to water, its presence is not harmful. A chloroform solution of the amine may be added drop-wise to a boiling chloroform solution of the thiophosgene<sup>505</sup> or to a stirred suspension of it in water.<sup>472</sup> The isothiocyanates of *p*-aminobenzenesulfonic acid<sup>1174</sup> and 4-antiprylamine<sup>1704.5</sup> have been prepared in this way. This is an excellent method for preparing mustard oils, but unfortunately the thiophosgene is not readily available.<sup>48, 125, 241, 330, 468, 469, 470, 471, 472, 474, 493, 505, 521, 530, 712, 796, 819, 856, 858, 859, 863a, 925, 1172, 1337, 1660</sup>

Two equations can be written which, if they could be realized, would make the preparation of alkyl isocyanates and isothiocyanates very simple:



Actually, CS<sub>2</sub> does convert an amine to the isothiocyanate, but only by way of a substituted thiourea or a dithiocarbamate. For example, the potassium dithiocarbamate, from the amine and carbon disulfide, is treated with ethyl chloroformate<sup>946</sup> to give the carbethoxydithiocarbamate, which decomposes:



The second step of this progression has been improved by base-catalyzed decomposition of the intermediate carbethoxydithiocarbamate derivative.<sup>809</sup> The preparation of these compounds has been discussed at length in Chapter 1 of Volume V, to which reference should be made. An isothiocyanate results from the elimination of ammonia from a substituted thiourea, or of hydrogen sulfide from a dithiocarbamic acid:



As the substituted thioureas are commonly prepared from the amine salts of the dithiocarbamic acids, they may be considered as intermediates. Simply heating a substituted ammonium dithiocarbamate for a long time under atmospheric pressure<sup>789b, 904, 1302, 1680, 1936</sup> or reduced pressure<sup>1559</sup> may produce the isothiocyanate. Aryl thioureas, when heated in chlorobenzene at 150° readily

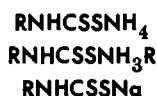
undergo fission into ammonia and good yields of aryl isothiocyanates.<sup>116</sup>

Compounds that combine with or react with  $\text{NH}_3$  or alkyl amines may aid in the separation of these from substituted thioureas. For this purpose, hydrogen chloride,<sup>186, 813, 814</sup> phosphorous pentoxide,<sup>813, 814, 1233</sup> hydriodic acid,<sup>1531a, 1805</sup> 70% sulfuric acid,<sup>1075, 1122</sup> phosphoric acid,<sup>813, 814, 1671</sup> acetanhydride,<sup>107, 196, 238, 851, 941a, 1867, 1868</sup> acid chlorides,<sup>401</sup> ethyl chloroformate,<sup>34c, 917, 925, 946, 1258a, 1917</sup> and phosgene<sup>454, 1495, 1673</sup> have been recommended, each to be used under appropriate conditions. Heptylidene diisothiocyanate,  $\text{C}_6\text{H}_{13}\text{CH}(\text{NCS})_2$ , has been prepared from the thiourea derivatives,  $\text{C}_6\text{H}_{13}\text{CH}(\text{NHCSNH}_2)_2$ , with the aid of hydrochloric acid.<sup>1570</sup>

The formation of isothiocyanates by eliminating hydrogen sulfide from substituted dithiocarbamic acids, as represented in the immediately preceding equation, is imaginary, because these acids are not known in the free state. Actually the isothiocyanate is formed by splitting off a hydrosulfide, or sulfide, from the heavy metal salt:



The heavy metal salts are obtained by double decomposition from the relatively stable ammonium, alkyl ammonium, and sodium dithiocarbamates,



which have been described in Volume IV:



Practically, a solution of the heavy metal salt is added to a solution of one of the dithiocarbamate salts just named and the mixture is steam-distilled.<sup>615f, 769a</sup> The isothiocyanate passes over. Silver,<sup>813, 814, 817, 897b, 1291, 1424a, 1531b, 1531c, 1672, 1772</sup> mercuric,<sup>41, 615f, 769a, 813, 814, 817, 897b, 1291, 1424a, 1531b, 1531c, 1672, 1772</sup> copper,<sup>456, 569, 1147</sup> ferric,<sup>675, 1843, 1862b</sup> and lead<sup>396, 399, 412b, 481, 673, 773</sup> salts have been used; basic lead acetate is preferred on account of cost. This method is particularly applicable to the preparation of aryl isothiocyanates.<sup>773</sup> The addition of an oxidising agent with the lead nitrate is said to be beneficial.<sup>994</sup>



Examples are given of the preparation of the isothiocyanates starting with cyclohexylamine,<sup>1672</sup> campholyl amine,<sup>506, 559</sup> and of the diisothiocyanates from ethylenediamine,<sup>1917</sup> decamethylenediamine,<sup>1918</sup> and bis(4-aminocyclohexyl) methane.<sup>1003</sup>

The H<sub>2</sub>S may be eliminated by oxidation with alkaline sodium hypochlorite.<sup>1581, 1585</sup> Organic isothiocyanates are formed when an alkali hypohalite solution is added slowly to a solution or emulsion of the ammonium salt of an N-monosubstituted dithiocarbamic acid in water and methylene chloride.<sup>1579.5</sup>

### Other Syntheses

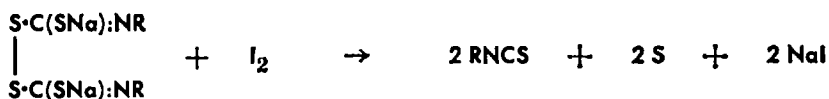
The reaction of iodine<sup>813, 814, 816, 1531a</sup> or chlorine<sup>1184</sup> with a dithiocarbamate gives an isothiocyanate:



The dithiocarbamate may be considered as decomposing:



The sodium salt of a thiuram disulfide gives a mustard oil when treated with iodine: <sup>222a, 222d, 223, 232, 1184, 1578, 1597</sup>



Mild oxidation of isothiuram disulfide gives a mustard oil.<sup>222c, 1595</sup>

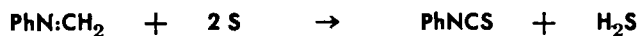
Furylethylene added drop-wise to a solution of thiocyanogen and heated gave 2-(1-isothiocyanato-2-isothiocyanoethyl) furan.<sup>1075.7</sup>

An alkyl isocyanate can be converted to the isothiocyanate by phosphorous pentasulfide: <sup>1242</sup>



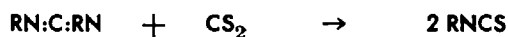
An isothiocyanate is formed by the reaction of cyanogen chloride with a dithiocarbamate from a primary amine.<sup>351, 1682</sup>

Heating an amine formaldehyde compound with sulfur gives a mustard oil: <sup>985</sup>



Phenyl isothiocyanate also results from the treatment of phenyl azide, dissolved in carbon disulfide, with aluminum chloride.<sup>206</sup>

Isothiocyanoacetic acid can be obtained from chloroacetic acid, but only indirectly. Chloroacetic acid is condensed with thiourea to give the hydrochloride of a thiohydantoin, which is then hydrolyzed.<sup>1020</sup> An isothiocyanate is formed by the reaction of carbon disulfide with carbodiimide: <sup>1862a</sup>



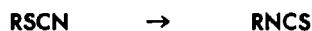
And by the addition of sulfur to a carbenzylamine: <sup>1862a</sup>



Organosilicon isothiocyanates are prepared by the interaction of silver isothiocyanate and the alkyl chloro (or iodo) silanes.<sup>27, 28, 245, 478</sup> Phenyl silicon isothiocyanates have been prepared through the reaction of silver isothiocyanate and phenylchlorosilanes.<sup>27</sup>

### REACTIONS OF ISOTHIOCYANATES

In the introduction to the reactions of thiocyanates it was pointed out that the radical attached to the sulfur in the thiocyanate, RSCN, remains with the sulfur through almost all of its reactions. In an isothiocyanate, RNCS, the radical is even more firmly attached to the nitrogen and stays with it no matter what happens to the —CS group. In the isomerizing of a thiocyanate to an isothiocyanate



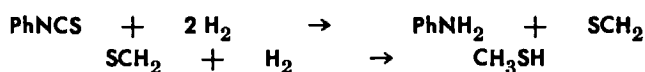
the alkyl leaves the sulfur to attach itself to the nitrogen. Several reactions were noted in which R—SCN reacts as an alkyl halide involving scission of the R—S bond.

The chief reactions of the isothiocyanates are those that involve breaking of the RN=CS bond or additions to the double bonds—the latter being far more important.

### BREAKING THE RN=CS BOND

#### *Reduction*

This reaction has been relied on to distinguish between thiocyanates and isothiocyanates. There is no mistaking a mercaptan for an amine. In the reduction of phenyl isothiocyanate with an aluminum amalgam, however, mercaptan is formed in a side reaction: <sup>717</sup>

*Oxidation*

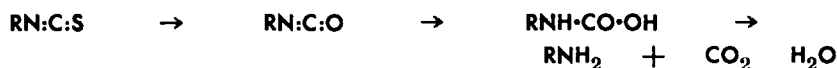
The isotopic exchange which takes place between RNCS and  $\text{KS}^{35}\text{CN}$  shows that the sulfur may be removed without disturbing the rest of the molecule.<sup>1786</sup>

The oxidation of an alkyl isothiocyanate may take various courses depending on the nature of the oxidising agent, the acidity or alkalinity of the solution, and other conditions. Barium hydroxide, and mercuric or lead oxide in water suspension may remove the sulfur. The fact that allyl mustard oil gives diallyl urea<sup>256, 268a, 268b, 1668</sup> indicates that there must be partial hydrolysis and recombination of the amine to form the diallyl urea. The sulfur commonly goes to the sulfate ion.<sup>1142b</sup>

Phenyl isothiocyanate is converted to azobenzene by treatment with  $\text{H}_2\text{O}_2$ :<sup>713</sup>



According to circumstances the sulfur of an alkyl isothiocyanate is oxidised by nitric acid to sulfur dioxide or to sulfuric acid, and the carbon of the  $-\text{N}:\text{C}:\text{S}$ , to carbon dioxide. The  $\text{RN}-$  may appear as a salt of the amine  $\text{RNH}_2$ .<sup>813, 814, 1668</sup> It seems curious that both oxidation and reduction should give the amine. It may be that this is the result of hydrolysis of an unstable carbamic acid:



Dry chlorine converts ethyl isothiocyanate in ether solution to a white powder, which when treated with alkali, forms a cyclic compound,  $(\text{EtNCS})_2\text{O}$ , melting at  $42^\circ$ .<sup>1631</sup> Bromine gives this product in presence of water.<sup>574</sup>

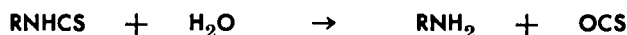
Allyl, methyl, and ethyl isothiocyanates are desulfurized by heating with triethylphosphine:<sup>813, 814</sup>



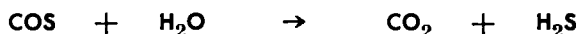
The allyl may be made to combine with triethylphosphine<sup>813, 814</sup> and with triethylstibine.<sup>1566</sup> A mustard oil is converted to a nitrile by heating with a metal.<sup>117b</sup>

### Hydrolysis

The hydrolysis of mustard oils is a convenient method for preparing amines, some of which are not otherwise readily available. This hydrolysis may be effected by heating with water at 200° C, or preferably by refluxing with dilute acids.<sup>425, 813, 814</sup> It serves well for the preparation of allylamine.<sup>171, 191</sup> The typical reaction is:

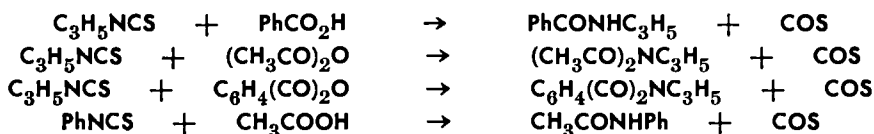


The carbon oxysulfide may be hydrolized further: <sup>615b, 1534</sup>

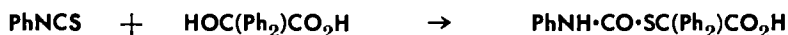


Heating allyl mustard oil with concentrated sulfuric acid has been used for the generation of carbon oxysulfide.<sup>1850</sup> When sulfuric acid is used in the preparation of allylamine, a part of the allylamine may be hydrated to hydroxypropylamine. For this reason hydrochloric acid is preferred.<sup>609</sup> Allylamine has been obtained in 75% yield by refluxing allyl mustard oil with 4 parts of 20% hydrochloric acid until the oil layer disappears. The resulting solution is concentrated and the amine liberated with sodium hydroxide.<sup>1098</sup>

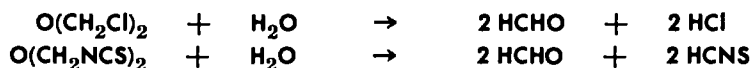
Allyl ammonium oxalate results when allyl mustard oil is boiled with aqueous oxalic acid.<sup>659</sup> With other organic acids or anhydrides, carbon oxysulfide is eliminated, and an acyl derivative of allylamine remains: <sup>813, 814, 986, 1867</sup>



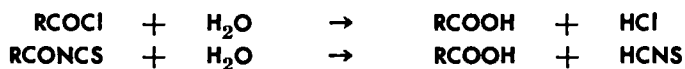
As the hydroxyl group of benzylic acid is more active than the carboxyl, the product is a phenylthiourethane derivative: <sup>124</sup>



The R—N bond in an isothiocyanate is usually so firm that the nitrogen remains with the radical, but this bond is labilized by the presence of oxygen on the alpha carbon atom. Thus, bis(isothiocyano)methyl ether is a formaldehyde derivative analogous to dichloromethyl ether. The two compounds are hydrolyzed similarly: <sup>783</sup>



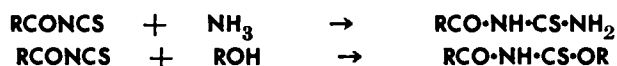
An acyl isothiocyanate,  $\text{RCO}\cdot\text{NCS}$ , resembles an acid chloride,  $\text{RCO}\cdot\text{Cl}$ , from which it is prepared. Hydrolysis follows the same course in both: <sup>438</sup>



An acyl isothiocyanate may react this way with aniline: <sup>438</sup>

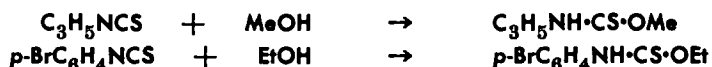


or, like any other isothiocyanate, and add ammonia or an alcohol: <sup>438, 439, 443</sup>



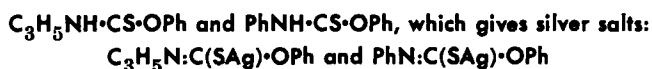
#### ADDITION TO $\text{SC}=\text{NR}$ DOUBLE BOND

An alcohol unites with a mustard oil to form a thiourethane: <sup>62, 329, 438, 813, 814, 913, 1346, 1595, 1672, 1920</sup>



When the mustard oil is added to a suspension of a sodium alcoholate in xylene <sup>1529</sup> the sodium derivative,  $\text{RNNa}\cdot\text{CS}\cdot\text{OR}$ , is formed. This is hydrolyzed to the thiourethane. It is claimed that methyl, ethyl, and other isothiocyanates can be combined with cellulose. <sup>1130</sup> Benzoyl isothiocyanate and ethylene chlorhydrin give  $\beta$ -chloroethyl benzoyl thiocarbamate. <sup>1920</sup> On account of its reaction with alcohol, oil of mustard kept in alcoholic solution may become therapeutically inert. <sup>266</sup> The rates of reaction of a large number of substituted phenyl mustard oils with ethanol have been compared. <sup>253</sup>

Phenols react like alcohols with allyl and phenyl isothiocyanates, forming the thiourethanes:



The silver atoms in these can be substituted by alkyls. <sup>1600</sup> In the presence of hydrogen chloride, the thiophenylurea from allyl mustard oil and phenol condenses to 3-methyl-2-(4-hydroxyphenyl)thiazoline. <sup>753, 1320</sup>

A mustard oil combines with sodium hydrosulfide to make a sodium dithiocarbamate: <sup>1892b</sup>



From the sodium salts other salts may be prepared, such as:



The copper, nickel, cobalt, and ferric salts are colored. <sup>412a</sup> The addition of hydrogen sulfide should give the dithiocarbamic acid:

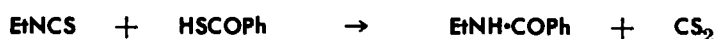


This acid is unstable, so the actual products are  $\text{RNH}\cdot\text{CS}\cdot\text{NHR}$  and  $\text{CS}_2$ . <sup>1448</sup>

A mercaptan adds as would an alcohol: <sup>586</sup>



The addition product of mercaptoacetic acid with allyl or methyl isothiocyanate condenses to the 2-thio-3-alkyl-4-keto-thiazolidine. <sup>34d, 35a, 35b</sup> Allyl mustard oil reacts with cysteine to form  $\alpha$ -N-allylthiocarbamido- $\beta$ -mercaptopropionic acid. <sup>1787</sup> A substituted amide is formed from the reaction of an isothiocyanate and  $\text{HSCOPh}$ : <sup>912b</sup>



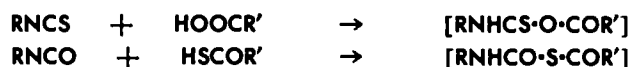
Considering the thiobenzoic acid as a mercaptan, the first reaction would be:



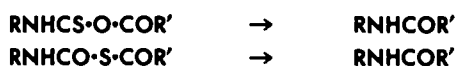
Carbon disulfide would be eliminated:



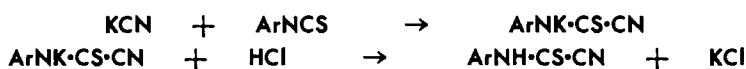
The reactions of an alkyl isothiocyanate with a carboxy acid and of an alkyl cyanate with a thio acid would be:



Carbon oxysulfide would be eliminated from these intermediates, leaving substituted amides: <sup>1050</sup>



The compounds  $\text{ArNHCSCN}$  are obtained by the action of potassium cyanide on aromatic mustard oils<sup>1483</sup> followed by acidification:



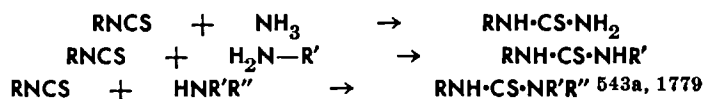
Potassium bisulfite adds to allyl mustard oil: 191, 1523a



Methyl, propyl, isopropyl, butyl, isobutyl, and benzyl isothiocyanates react with potassium pyrosulfite to give the salts  $\text{RNH}\cdot\text{CS}\cdot\text{SO}_3\text{K}$ .<sup>75</sup>

#### ISOTHIOCYANATES WITH AMINES

A characteristic reaction of isothiocyanates is their reaction with ammonia, primary, or secondary amines:



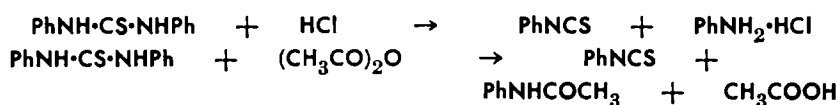
to give substituted thioureas.<sup>34a, 71, 143, 268a, 268b, 330, 397, 615b, 696, 769b, 805, 813, 814, 863b, 903b, 1225, 1242, 1292, 1531b, 1534, 1549, 1570, 1716, 1813, 1815</sup>

As stated earlier, this reaction was discovered in the study of natural oil of mustard: 54, 158a, 780b, 1143, 1668



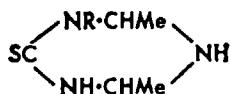
That this reaction takes place in solution can be shown by various physical methods.<sup>787, 1055, 1070, 1071, 1252, 1794, 1795, 1836, 1940, 1941</sup>

To prepare methyl thiourea, 95 g of methyl mustard oil is added to 140 cc of conc ammonium hydroxide during 1 hour and the excess of ammonia removed by heating on the water bath for 30 min; yield 74–81%.<sup>1258b</sup> This reaction may be reversed as in the treatment of diphenyl thiourea by hydrochloric acid<sup>814</sup> or acetanhydride: 1866



One molecule of an alkyl isothiocyanate reacts with two of aldehyde ammonia to give a crystalline compound of undetermined structure, which on boiling with water gives off aldehyde

and ammonia, leaving the alkyl thiourea.<sup>1571c</sup> The structure has been written provisionally: <sup>438</sup>



Many of the examples of the preparation of disubstituted thioureas from isothiocyanates and amines have been discussed in Chapter 1 of Volume V. A few additional examples are noted here. Allyl mustard oil reacts with amines of the camphor group and camphyl isothiocyanate with amines.<sup>506, 673</sup> Allyl mustard oil has been made to react with 1-carbethoxy-2-aminopropylene,<sup>778</sup> 3-chlorobutylamine,<sup>1151</sup> aminothiazoline<sup>589, 1804</sup> anthranilic acid,<sup>1525</sup> semi-carbazide and piperazine,<sup>1523b</sup> oximes,<sup>634a, 634b, 642, 643, 644</sup> and methylhydrazine.<sup>278</sup>

1-Methyl-2-hydroxybutyl ethyl thiourea,  $\text{EtCH(OH)CHMe-NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{Et}$ , has been obtained from ethyl isothiocyanate and the amine.<sup>896</sup>

Thioureas have been prepared from methyl isothiocyanate with ethyl- $\beta$ -aminocrotonate,<sup>129</sup>  $\beta$ -bromopropylamine,<sup>806</sup> 5-methylamino-1,3-dimethylhydantoin,<sup>160, 162, 192</sup> and ethyl  $\beta$ -amino- $\alpha, \beta$ -dimethylacrylate;<sup>236</sup> and from phenyl isothiocyanate with methylpropyl amine<sup>1716</sup> diethylaminoethylamine,<sup>1501</sup> N-phenylethanolamine,<sup>398</sup> toluidines,<sup>594</sup> 2- $\mu$ -aminooxazoline,<sup>590</sup> isatinic acid,<sup>1484</sup> 3-methyl-5-amino-1,2,4-triazole,<sup>519</sup> 1,2-*bis*-(benzylamino) ethane,<sup>1137</sup> and 1,10-*bis*-(aminoethylamino) decane.<sup>22</sup>  $p\text{-ClC}_6\text{H}_4\text{NCS}$  and  $p\text{-FC}_6\text{H}_4\text{NH}_2$  heated together give N-(4-chlorophenyl)-N'-(4-fluorophenyl) thiourea.<sup>878</sup>

Benzidine heated with excess allyl mustard oil forms the double thiourea which decomposes with elimination of allyl amine: <sup>315</sup>



From  $\alpha$ -aminoaceto nitrile and aryl and alkyl isothiocyanates the final products are substituted thiazoles.<sup>369</sup>

Several triple thioureas have been prepared from 1,3,5- $\text{C}_6\text{H}_3(\text{NCS})_3$ .<sup>125</sup> Phenyl mustard oil does not react with an aniline which contains two *ortho* substituents, or a nitro group in the *ortho* or *para* positions.<sup>667</sup> A study has been made of the preparation of substituted thioureas from *p*-methyl, *p*-nitro, *p*-chloro,



*p*-bromo, and *p*-iodo-phenyl mustard oils.<sup>530</sup> Phenyl,<sup>1335</sup> *o*-tolyl,<sup>1335</sup> *m*-nitrophenyl,<sup>1548</sup> *p*-bromophenyl,<sup>1547</sup> *p*-bromobenzoyl,<sup>335</sup> *p*-phenylphenyl<sup>238</sup> and  $\alpha$ -naphthyl<sup>1730</sup> isothiocyanates have been recommended for the identification of aromatic amines.

Phenyl isothiocyanate has been used in the study of the degradation of polypeptides, and for identifying the end groups in hemoglobins and tobacco mosaic virus.<sup>485, 1606</sup> *p*-Iodophenylisothiocyanate has been used as a reagent for the determination of peptide structure.<sup>283</sup> An acyl isothiocyanate, RCONCS, combines with a primary amine to give an acyl thiourea<sup>438, 439, 441a, 443b, 448, 589, 836, 1244a</sup> Thiocyanated acyl thioureas result when acyl mustard oils react with thiocyano amines.<sup>835b</sup>

Isothiocyanates react with diaryl guanidines<sup>1664</sup> and with monomeric or polymeric alkyleneimines.<sup>510, 870</sup>

A sulfonamide reacts as if it were an amine:<sup>1395</sup>



Aromatic isothiocyanates were treated with oximes<sup>634b, 1369</sup> to yield  $\text{R}_2\text{C}:\text{NOC}(\text{S})\text{NHAr}$ . *p*-Phenylazophenyl isothiocyanate yields the expected oxime thiocarbanilide.<sup>645</sup> With hydrazine hydrate and substituted hydrazines,<sup>577, 707, 708, 1452</sup> isothiocyanates give thiosemicarbazides:



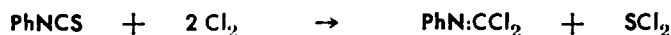
This is the subject of Chapter 2 in Volume V. The colored thiosemicarbazides formed in the reaction between isothiocyanates and the 2,4-dinitrophenylhydrazine have been used for the chromatographic separation and identification of certain isothiocyanates.<sup>547</sup>

The reactivities of the amino groups of various amino acids have been compared by measuring the reaction velocities with phenyl isothiocyanate.<sup>1541</sup>

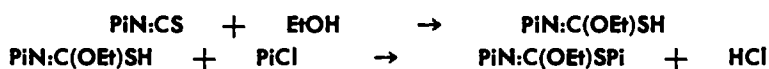
#### OTHER REACTIONS

Allyl mustard oil and sodium azide react to give 1-allyl-5-mercaptotetrazole. The 1-phenyl derivative is from phenyl isothiocyanate.<sup>1719</sup>

Chlorine chlorinates both the carbon and the sulfur of an isothiocyanate:<sup>774, 1632</sup>

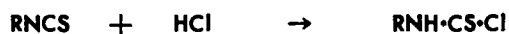


When picryl chloride is added to a hot solution of ammonium thiocyanate in ethanol, there is an immediate precipitation of a compound  $\text{PiN}\cdot\text{C}(\text{OEt})\text{SPi}$ . This is explained by assuming: <sup>385, 386</sup>

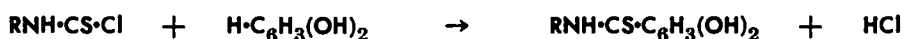


If bromine is added to methyl isothiocyanate, hydrogen sulfide passed in, and the base set free by sodium carbonate, 2-4-dimethyl-3-thio-5-keto-1,2,4-thiadiazolidine is obtained. <sup>575</sup> The diethyl derivative is from ethyl mustard oil. <sup>576</sup>

Hydrogen chloride combines with an isothiocyanate to give an acid chloride isomeric with the above:



With a polyhydroxy benzene this reacts as an acid chloride: <sup>952</sup>

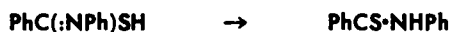


With phenol the reaction takes place only in the presence of aluminum or zinc chloride. <sup>1215, 1504</sup>

The Grignard reagent adds to the  $=\text{C}:\text{S}$  of an isothiocyanate:



Alkylation by methyl sulfate gives  $\text{PhN}:\text{CPhSMe}$ , showing that the  $-\text{MgBr}$  adds to the sulfur. Acidification before methylation yields the thioanilide. The isothioanilide, which must be the primary product, isomerizes to the thiobenzanilide: <sup>183, 652, 1389, 1542</sup>



As would be expected, thiobenzanilide results from the reaction of phenyl sodium, or phenyl lithium, on phenyl mustard oil. <sup>650</sup> Similarly, thiovaleric anilide,  $\text{BuCS}\cdot\text{NHPh}$ , is formed by the reaction of butyl magnesium bromide. <sup>1914</sup> Sodium phenylacetylide reacts as a Grignard reagent with *p*-tolyl mustard oil, giving phenylthiopropiolic toluidine,  $\text{PhC}:\text{C}\cdot\text{CS}\cdot\text{NHC}_6\text{H}_4\text{Me}$ . <sup>1914</sup>

The addition of the sodium derivative of malonic ester to allyl mustard oil may be considered as following the same course. The final result is the N-allyl amide of a thio-acid: <sup>1241b, 1533a</sup>



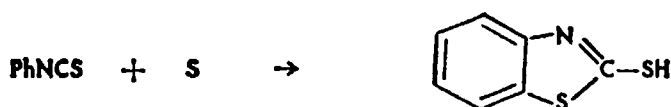
Methyl and phenyl isothiocyanates react analogously with the sodium derivatives of malonic ester, acetoacetic ester, and diacetylmethane.<sup>646, 1914</sup> With sodium cyanamid the addendum is  $\text{NH:C:NNa}$  and the product is a mono-sodium salt,  $\text{RNH}\cdot\text{CS}\cdot\text{NNa}\cdot\text{CN}$ , which when alkylated with  $\text{R'I}$  gives a dialkyl cyanothiurea,  $\text{RNH}\cdot\text{CS}\cdot\text{NR'CN}$ .<sup>769, 1915.5</sup> A number of these are in the tables at the end of Chapter 1, pages 99–101.

An alkyl thiocyanate oxidises sodium arsenite to arsenate, whereas an isothiocyanate forms a thioarsenate.<sup>719</sup>

In the presence of aluminum chloride, an isothiocyanate reacts with benzene to give an N-substituted thiobenzamide: <sup>583, 1807</sup>



2-Mercaptobenzothiazole is formed when phenyl isothiocyanate is heated with sulfur to  $230^\circ \text{C}$ .<sup>893</sup>



The addition of bromine to allyl mustard oil gives  $\beta,\gamma$ -dibromopropyl isothiocyanate.<sup>438, 1788</sup> 5-Bromomethyl-2-hydroxy-4-thiazoline is produced by the action of any alcohol on this,<sup>736</sup> instead of the 2-alkoxy- as was formerly supposed.<sup>438, 607a</sup> Chlorine gives a crystalline compound which can be sublimed.<sup>215a</sup> There is evidence for the addition of iodine, but the product can not be isolated.<sup>1207</sup> The addition of olefins to phenyl isothiocyanate has been studied as to relation between substitution and composition of the equilibrium mixture.<sup>90</sup>

### Determination of Mustard Oil

As allyl isothiocyanate is the valuable constituent in mustard seed and in mustard preparations but may be objectionable in other materials such as pressed cake designed for cattle feed,<sup>33c, 56</sup> considerable attention has been given to its detection and estimation. The seeds from which oil of mustard<sup>305</sup> is obtained contain also 25–30% of a non-volatile oil which may be classed with other seed oils.<sup>526, 695, 822</sup> Calculated on the weight of the seed, the amount of volatile oil of mustard which can be obtained

runs from 0.25 to 1.25% according to variety and origin.<sup>298, 299, 465b, 873, 1029</sup> of the seed.

The allyl isothiocyanate in oil of mustard can be identified by the thiosinamine that results when the oil is treated with ammonia:



This is monoclinic<sup>1935</sup> and gives characteristic crystals which may be examined under the microscope.<sup>1523c</sup> The presence of allyl isothiocyanate may be shown by adding phenylhydrazine which gives a positive test with one drop of a 0.00002% solution.<sup>1411</sup>

As has been stated in an earlier section, a mustard oil is not present in the seed as such, but as a constituent of the glucoside, myrosin, so the first step in the assay of mustard seed is maceration with water at 70°<sup>57</sup> to effect hydrolysis of the myrosin.<sup>1397a, 1893b</sup> Some ethanol is commonly added<sup>298, 1470</sup> though it has been stated that the hydrolysis is six times as rapid in its absence as in its presence.<sup>364</sup> As has been mentioned in a previous section, the strength of *Spiritus sinapis* may change with time on account of the reaction of the ethanol with the allyl isothiocyanate.<sup>1659</sup> The second step, extracting the volatile oil of mustard out of hydrolyzate, is usually effected by steam distillation.<sup>442</sup>

The oil in the distillate may be oxidised with permanganate,<sup>1575b</sup> bromate,<sup>1181</sup> or with bromine,<sup>309</sup> and the sulfur determined as barium sulfate;<sup>459, 706</sup> or the mustard oil may be reduced by zinc dust to allyl amine, which may be caught in sulfuric acid and determined.<sup>1375</sup> Any carbon disulfide that may be in the oil is converted to xanthate and titrated.<sup>155</sup> An isothiocyanate can be hydrolyzed and the amine estimated:<sup>990</sup>



The mustard oil in the steam distillate may be converted by ammonia into thiosinamine which can be determined by any of several methods. It may be weighed as such<sup>932</sup> or the solution containing it evaporated down and nitrogen determined in the residue by the Kjeldahl method.<sup>932</sup> The thiourea may be desulfurized by mercuric,<sup>557b, 1106</sup> or silver oxide.<sup>34b, 435, 754, 1149, 1837</sup> The mercuric sulfide and the silver sulfide can be weighed. Thiosinamine can be determined iodometrically<sup>1268</sup> by adding an

excess of standard iodine solution and titrating back with thio-sulfate.<sup>1223</sup>

Though there have been many variations in details, the most widely used method of analysis is to catch the distillate containing the mustard oil in ammoniacal standard silver nitrate. After a suitable interval of time, during which the solution may be heated, the precipitated silver sulfide is filtered off and the excess silver nitrate titrated.<sup>214, 244, 298, 299, 364, 615d, 1067a, 1387, 1470, 1514, 1611</sup> This method has been developed for micro-determination.<sup>1271</sup> Instead of steam distillation, air may be passed through the warm mixture to carry the volatile oil over into an oxidising solution, such as potassium permanganate, to convert the sulfur to the sulfate ion which can be weighed as barium sulfate.<sup>437</sup> Allyl isothiocyanate in wine distillates is detected by silver nitrate or by the formation of thiosinamine.<sup>1430</sup> Air containing it is aspirated through ethanol and the mustard oil titrated with silver nitrate.<sup>639</sup> The mustard oil may be determined volumetrically by salting it out with ammonium sulfate and collecting it in a narrow graduated tube.<sup>940, 1515</sup>

Methods of analysis have been reviewed.<sup>375, 391, 615d, 615e, 639, 698, 766, 1105, 1469, 1557, 1575a, 1611, 1702, 1825, 1826, 1891</sup> The odors and constitutions of various mustard oils have been tabulated together with specifications from various pharmacopeias.<sup>468a</sup>

### Physiological Effects of Isothiocyanates

Attention has been centered on allyl isothiocyanate on account of its well-marked properties and its frequent occurrence in vegetable products. The poisoning of cattle by the heat-sensitive<sup>255</sup> rape seed oil cake<sup>584, 1061, 1605</sup> and the epidemic dropsy<sup>465a, 1078, 1079</sup> have been attributed to it. Marked effects follow the ingestion of it.<sup>66, 1239b, 1511</sup> Mustard oil influences the resorption of fats in the small intestine,<sup>909, 1750</sup> dilates the arterioles and capillaries,<sup>1339</sup> causes the liberation of histamine,<sup>726</sup> and irritates the skin.<sup>556, 560b</sup> Its physiological effect is supposed to be due to reaction with free sulfhydryl groups.<sup>81</sup> When small doses of it are fed to a pig, most of the sulfur appears in the urine.<sup>1397b</sup> Mustard oil causes redness, miosis, and chemosis of the rabbit's eye,<sup>685, 1283</sup> and it is toxic when injected intravenously into animals.<sup>373, 821</sup> Cases of vesication in laboratory and industrial

workers have been reported for isopropyl<sup>672</sup> and methyl isothiocyanates<sup>672</sup> and for  $C_9H_{17}NCS$ .<sup>1617</sup>

Allyl,<sup>29</sup> *m*-allyloxyphenyl,<sup>819, 1696</sup> *m*-propoxyphenyl<sup>817.5</sup> methyl and propyl isothiocyanates<sup>23</sup> have pronounced anthelmintic activity in men and animals.<sup>1927</sup> The ascaricidal action of 38 aromatic isothiocyanates and related compounds have been compared.<sup>949</sup> The hyperemic properties of a group of mustard oils were evaluated in clinical tests. The benzyl was the most active.<sup>636</sup>  $\alpha$ -Naphthylisothiocyanate exerts antithyroid effect on the guinea pig,<sup>1217</sup> inhibits metamorphosis of tadpoles,<sup>1217</sup> and increases the weight of the spleen in rats.<sup>1219</sup> The influence of allyl isothiocyanate on the activity of papain in the presence of cyanide or of cysteine has been studied and a mechanism proposed.<sup>424, 545</sup> Sterol isothiocyanates have been studied for their glucocorticoid activity.<sup>326</sup>

The effects on yeast have been investigated.<sup>668, 846, 1131, 1304, 1317</sup> Allyl isothiocyanate does not influence the autolysis of yeast;<sup>1304</sup> ethyl and phenyl isothiocyanates inhibit its growth.<sup>668</sup> Mustard oil diminishes the action of urease,<sup>545, 895</sup> acts as a preservative for blood,<sup>1550</sup> and prevents fermentation,<sup>1185</sup> the formation of mycoderma in beer,<sup>1763</sup> and the growth of bacteria,<sup>184, 377, 560a, 560b, 668, 725, 833, 898, 1185, 1261</sup> inhibits the oxidation of ascorbic acid<sup>74a, 74b, 1543</sup> and counteracts the virulence of mosaic tobacco virus.<sup>602</sup> Benzyl, isobutyl, and allyl isothiocyanate inhibit the transaminase that catalyses the formation of alanine and  $\alpha$ -ketoglutaric acid from glutamic and pyruvic acids.<sup>407</sup> There appears to be a rough correlation between this inhibition and antistaphylococcal activity of isothiocyanates.<sup>407</sup> Allyl mustard oil increases the rate of mutation of *Drosophila melanogaster*<sup>65</sup> and in general has a weak mutagenic effect.<sup>64, 583</sup> Allyl and  $\beta$ -phenylethyl isothiocyanates stimulate germination of spores.<sup>831</sup>

Allyl mustard oil is inactivated by cysteine, glutathione, and mercaptans<sup>81</sup> and has no influence on the rate of growth of tumor cells.<sup>565</sup> When injected subcutaneously, ethyl isothiocyanate is somewhat less toxic to the rat than is the allyl compound.<sup>1107</sup> 2-Phenylethyl mustard oil has been compared with the allyl as to toxicity.<sup>833</sup>

The methyl and ethyl resemble the allyl in bactericidal properties.<sup>560b</sup> Allyl isothiocyanate<sup>1044</sup> and certain substituted thio-

cyano organics have been tested as bactericidal agents.<sup>406b, 523, 596, 600</sup> A mixture of allyl mustard oil and trichlorethylene has been claimed as a disinfectant.<sup>725</sup> The structure and antimicrobial activity of some isothiocyanates have been compared.<sup>219</sup> The reaction product of phenyl isothiocyanate with iodine trichloride is said to have antiseptic properties.<sup>1569</sup> The reaction products of ethylenimine with polyisothiocyanates are said to be useful in the treatment of carcinom.<sup>520</sup>

### Applications

Plastics are said to be obtained by the polymerization of unsaturated acyl isothiocyanates,<sup>17</sup> or of vinyl isothiocyanate with acrylonitrile,<sup>387</sup> acrylamide,<sup>387</sup> styrene,<sup>387</sup> acrylic acids,<sup>1120</sup> and also with alkyleneimine.<sup>509, 856, 858, 859, 1809</sup> A third constituent may be a protein,<sup>512, 856, 858, 859</sup> an albuminous substance,<sup>511</sup> a polyhydric phenol<sup>508</sup> or carbon disulfide.<sup>511</sup> Condensation polymers are said to be formed from polyisothiocyanates with hydroxylated polyvinyl resin<sup>462</sup> and organic-inorganic compounds;<sup>105, 814, 1245, 1254b, 1683, 1699</sup> and from hexamethylene diisothiocyanate<sup>653, 883</sup> with dihydric alcohol,<sup>308</sup> phenol,<sup>308</sup> alkyd<sup>463, 1526, 1527</sup> resin, polyether<sup>1527</sup> resins, cellulose esters,<sup>735</sup> low molecular weight polymers,<sup>141, 461</sup> and low polymers containing free amino- or hydroxyl groups.<sup>1777</sup> Adducts are formed by refluxing a hydroxylated inorganic compound, such as clay, with an alkyl isothiocyanate in an organic solvent.<sup>1254a</sup> Decamethylene,<sup>1433</sup> *p*-phenylene,<sup>1433</sup> and other diisothiocyanates<sup>461, 563</sup> have been suggested as constituents of formaldehyde condensation products. Isothiocyanates are said to be useful in the bonding of laminates.<sup>1432</sup>

Allyl isothiocyanate has been recommended for the refining of lubricating oils.<sup>535</sup> Butyl  $\alpha$ -isothiocyanoamyl ether in lubricating oils is said to prevent corrosion.<sup>1656</sup> The reaction product of an alkyl isothiocyanate with a halogenated castor oil is claimed as a pourpoint depressant.<sup>436</sup>  $\alpha$ -Naphthyl isothiocyanate improves the color of apples,<sup>1356</sup> and allyl isothiocyanate has been proposed as a preservative for fruit juices.<sup>1045</sup> Alkaline metal aurothiocyanates<sup>747</sup> and allyl mustard oil<sup>1148</sup> in very small concentrations sensitize photographic gelatin. Certain thiocyanates serve this purpose<sup>1030, 1677, 1864</sup> and some are stabilizers.<sup>1538</sup>

Phenyl mustard oil is claimed as a catalyst,<sup>1294</sup> and nitrosubstituted aromatic thiocyanates as retarders<sup>1946</sup> for the polymerization of butadiene.

Isothiocyanates have been claimed for use in a resinous adhesive<sup>1313</sup> and as an improvement in effectiveness of a copper-plating bath.<sup>1406</sup> Allyl isothiocyanate is claimed as a stabilizer for lead tetraethyl during steam distillation.<sup>289b</sup> Allyl isothiocyanate and some thiocyanates have been tested as dispersing agents for schooling fish.<sup>793</sup>

When (aminoalkyl)thiosulfuric acids are acylated with isothiocyanates the products, substituted alkyl thiosulfuric acids, are wetting, dispersing, and impregnating agents.<sup>187</sup>

### Perthiocyanic Acid

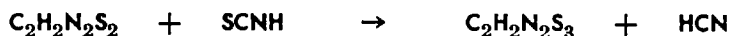
Perthiocyanic acid was discovered by Wöhler<sup>1901</sup> and studied by Voelckel<sup>1830a</sup> as a decomposition product of thiocyanic acid:



It can be isolated from the residue from the preparation of carbon oxysulfide by Than's method.<sup>550, 1766</sup> It is formed from ammonium thiocyanate and hydrochloric acid and is best purified through its barium salt.<sup>1018</sup>

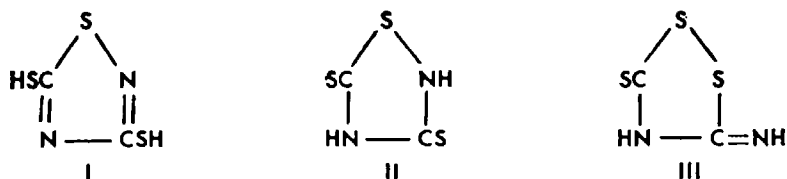
When 80% sulfuric acid is added to a 33% solution of ammonium thiocyanate a yellow coloration develops quickly and the solution now gives characteristic precipitates with metal ions, quite different from those obtained with a thiocyanate.<sup>1345a</sup> To prepare perthiocyanic acid, sulfuric acid is added to a concentrated solution of potassium thiocyanate and the mixture is kept cool. Potassium sulfate separates first and then the perthiocyanic acid.<sup>328</sup>

From its concentrated ether solution at 0° C, thiocyanic acid is transformed into perthiocyanic acid at a rate indicating a bimolecular reaction. The reaction has been followed for 600 hours. After a 5 hour incubation period hydrogen sulfide appears. The other by-product is hydrocyanic acid.<sup>165</sup> Dithiocyanic acid is believed to be an intermediate in the formation of perthiocyanic acid; it seems that it is sulfurized by a molecule of thiocyanic acid:





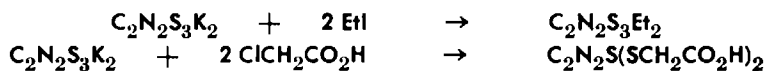
This acid is readily obtained but by processes which give no clue to its constitution. Its structure puzzled chemists for decades. It appears to exist in three forms, as shown below:



From I, the salts and esters are derived; II is the *pseudoacid*; and III is also known as *xanthane hydride*.<sup>658b, 658c, 658e, 745</sup> It has been suggested that the formation of perthiocyanic acid<sup>658b, 658c, 658e</sup> involves the two isomeric forms of thiocyanic acid.

When heated, perthiocyanic acid begins to decompose at 150°, with the production of hydrogen sulfide, thiocyanic acid, sulfur, and a residue that is soluble in alkali.<sup>1085</sup> Perthiocyanic acid is reduced by tin and hydrochloric acid to carbon disulfide and thiourea;<sup>328</sup> by sodium amalgam<sup>328</sup> to sodium carbonate, sodium sulfide, and ammonia; and by phosphorus triiodide and water to hydrogen sulfide, carbon disulfide, and thiourea hydroiodide.<sup>328</sup>

An ester of perthiocyanic acid results when its potassium salt is heated with an alkyl halide:<sup>1018</sup>



From ethylene bromide, a compound,  $\text{C}_6\text{H}_4\text{N}_2\text{S}_2$ , m. 150°, is the product. The formation and structure of this have not been explained.<sup>1370</sup>

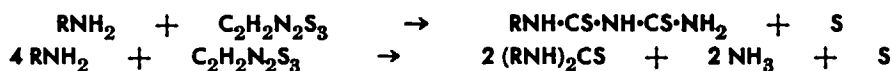
When ammonium thiocyanate is heated with acetic anhydride, carbon dioxide and oxysulfide, hydrocyanic acid, and hydrogen sulfide are evolved, while acetylperthiocyanic acid,  $\text{CH}_3\text{COHC}_2\text{N}_2\text{S}_3$ , remains.<sup>1315</sup> This can be obtained by refluxing perthiocyanic acid with acetanhydride.<sup>358</sup>

At 150–60°, ammonia, in excess, decomposes perthiocyanic acid into hydrogen sulfide, ammonium sulfide, and melamine thiocyanate.<sup>1421</sup>

Perthiocyanic acid unites with hydrazine to give 3,5-dithiol-1,2,4-triazole<sup>46, 47, 585, 591, 709, 1686</sup> and 5-amino-3-thiol-1,2,4-triazole. With phenylhydrazine, the products are 3,5-dithio-1-phenyl-1,2,4-triazole and 3-amino-5-thio-1-phenyl-1,2,4-triazole.<sup>591</sup>

Hydrogen sulfide is evolved from a boiling aqueous solution of perthiocyanic acid and hydroxylamine. On cooling sulfur separates and the solution contains thiocyanate ions.<sup>587</sup>

Perthiocyanic acid reacts with amines in various ways depending on the nature of the amine. Dithiobiurets, thioureas, or fused side rings may be formed:<sup>1811</sup>



When chlorine is passed into a solution of perthiocyanic acid sulfurmonochloride, cyanogen chloride, hydrochloric acid, and a brown body,  $\text{C}_5\text{N}_5\text{H}_3\text{S}_3\text{Cl}$ , are formed.<sup>1830c</sup>

Perthiocyanic acid is said to be useful in combating warm-blooded agricultural pests.<sup>1232</sup> In dosage of 0.1 to 0.2 g/lb of body weight it removed 100% of *Taenia* and 73% of *Dipylidium* but had little effect on hookworms. This dosage is not harmful unless repeated on consecutive days.<sup>501</sup> Its colored heavy metal salts have been recommended as pigments in paints and plastics.<sup>789a</sup>

### Dithiocyanic Acid

Dithiocyanic acid was given this name because it is formed from thiocyanic acid and has the composition of a dimer,  $\text{C}_2\text{H}_2\text{N}_2\text{S}_2$ . Its systematic name is cyanaminodithiocarbonic acid. There are two tautomeric structures: I,  $(\text{HS})_2\text{C}:\text{N}\cdot\text{CN}$  from which the salts and esters are derived; and II:  $\text{HSCS}\cdot\text{NH}\cdot\text{CN}$ , the free acid. The potassium salt crystallizes out in almost theoretical yield from a mixture of carbon disulfide, potassium hydroxide, and cyanamide<sup>745</sup> in ethanol.



Another way to prepare this salt is to grind 25 g of perthiocyanic acid with 19 g of potassium hydroxide<sup>1018</sup> in 23 cc of water, cooling with ice. The precipitated sulfur is filtered off and much absolute ethanol is added. The potassium salt comes out as an oil which solidifies after being washed with alcohol.<sup>745</sup>



When the calculated amount of hydrochloric acid is added to a solution of the potassium salt,<sup>745</sup> the free acid separates as unstable yellow needles.

The methyl ester,  $(\text{MeS})_2\text{C}:\text{N}\cdot\text{CN}$ , m.  $57^\circ$ , has been made from the silver salt and methyl iodide. When it is warmed with aqueous hydrochloric acid it combines with a molecule of water: <sup>745</sup>



The benzyl ester has been prepared from benzyl chloride and the potassium salt. Ammonia substitutes an amino group for one  $\text{PhCH}_2\text{S}$ —.



Ammonium sulphhydrate gives benzyl mercaptan and benzyl tri-thioallophanate,  $\text{PhCH}_2\text{S}\cdot\text{CS}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ , m.  $144^\circ$ .<sup>588</sup>

### Isodithiocyanic Acid

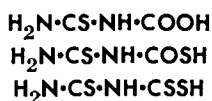
The potassium salt of isodithiocyanic acid was isolated from the residue from the preparation of carbon oxysulfide by Than's method. The free acid is only slightly soluble in cold water and can be recrystallized from hot. A number of its salts were prepared. Its ethyl ester, from the salt with ethyl bromide, is a red-brown liquid which breaks up on distillation<sup>550</sup> with the formation of ethyl disulfide. This obscure acid was later prepared by heating well-dried ammonium thiocyanate with acetic anhydride on the water bath. The structure  $\text{HN}:\text{CS}:\text{CS}:\text{NH}$  was assigned to it.<sup>918</sup>

Isodithiocyanic acid,  $(\text{HNCS})_2$ , is one of the products of treating thiocyanates with mineral acids.<sup>1717</sup>

The sodium salt, prepared by heating sodium cyanide with carbon disulfide, is claimed as a flotation agent.<sup>1103</sup>

### THIOALLOPHANIC ACID

Three thioallophanic acids are known: the mono-, di-, and tri-thio- forms. They are carboxy, thio-, and dithio-carboxy derivatives of thiourea:



The ethyl ester of monothioallophanic acid results from the addition of ammonia to carbethoxyisothiocyanate:

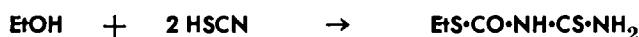


This can be recrystallized from hot water and melts at 140°. If amines are used instead of ammonia, N-substituted esters,  $\text{RNH}\cdot\text{CS}\cdot\text{NH}\cdot\text{CO}\cdot\text{OEt}$ , are obtained.<sup>443a</sup>

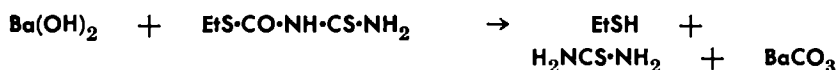
The isomeric ester,  $\text{H}_2\text{N}\cdot\text{C}(\text{:NH})\cdot\text{S}\cdot\text{CO}\cdot\text{OEt}$ , is from the reaction of ethyl chloroformate and thiourea.<sup>438</sup> An isomeric monothioaliphatic, not derived from thiourea, with the formula  $\text{H}_2\text{N}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{OEt}$ , has been prepared starting with thiocyanic acid.<sup>170</sup>

### DITHIOALLOPHANIC ACID

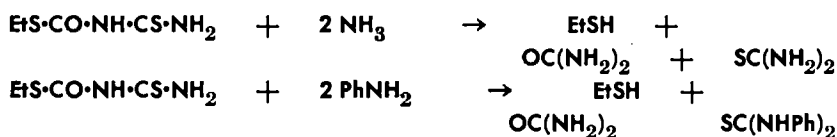
When concentrated hydrochloric acid is added to an alcoholic solution of potassiumthiocyanate, ethyl dithioaliphate separates as crystals, m. 170–5°:



This is hydrolyzed by barium hydroxide:

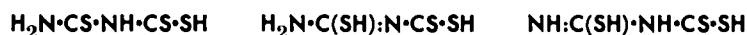


and also reacts with ammonia and with aniline:<sup>178</sup>



### TRITHIOALLOPHANIC ACID

There are three tautomeric formulae for trithioaliphatic acid:



This acid is derived from dithiocyanic acid by the addition of hydrogen sulfide to the  $-\text{CN}$  group: <sup>741b, 1519, 1522</sup>

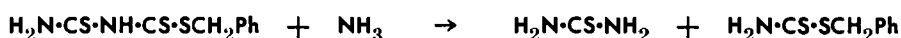


The potassium salt separates as yellow crystals when a concentrated solution of potassium dithiocyanate is saturated with hydrogen sulfide, under strong cooling. An almost quantitative yield is obtained from thiourea, carbon disulfide, and alcoholic potash:

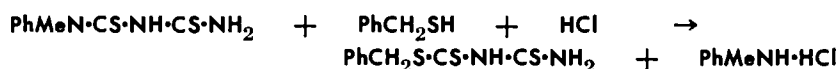


Alkylation of this salt produces esters: methyl, m. 164°, and

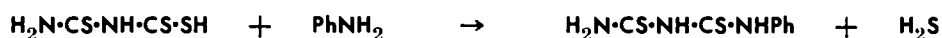
ethyl, m. 174°. The benzyl ester is split by ammonia into thiourea and benzyl dithiocarbamate: <sup>813, 814</sup>



The benzyl ester is produced by the action of benzyl mercaptan on phenylmethyldithiobiuret in presence of hydrogen chloride: <sup>585</sup>



A characteristic reaction of thio acids is the ready formation of anilids. Trithioallophanic acid reacts with aniline; <sup>658f</sup>



This anilid turns out to be phenyldithiobiuret. The oxidation to phenylthiuret is easily understood if the trithioallophanic acid is written in the tautomeric form: <sup>585</sup>



Free trithioallophanic acid decomposes easily into thiourea and carbon disulfide:



At higher temperatures hydrogen sulfide, thiocyanic acid, ammonia and sulfur are among the decomposition products. <sup>1085</sup>

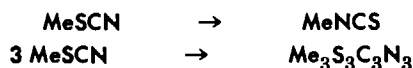
Certain of its esters have been claimed as corrosion inhibitors in lubricating oils. <sup>1820</sup>

### Thiocyanuric Acids

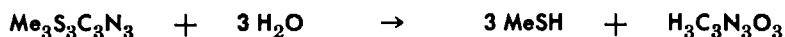
Dimethoxycyanuric chloride reacts with potassium hydrosulfide, giving the dimethyl ester of monothiocyanuric acid,  $(\text{CH}_3\text{O})_2\text{C}_3\text{N}_3\text{SH}$ , m. 174°. This hydrolyzes to the monothioacid,  $\text{C}_3\text{N}_3(\text{OH})_2\text{SH}$ , which decomposes at 316°. <sup>433</sup>

Cyanur-amino dichloride,  $\text{C}_3\text{N}_3\text{Cl}_2\text{NH}_2$ , is dissolved in alkali sulfide. On acidification, a white amorphous substance separates which has been identified as dithiomelanuric acid,  $\text{C}_3\text{N}_3(\text{SH})_2\text{NH}_2$ . <sup>432</sup> Monothiocyanuric acid is said to be useful in coating aluminum. <sup>1414</sup>

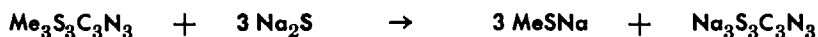
When methyl thiocyanate is heated, a part is isomerized and a part polymerized to the trimethyl ester of trithiocyanuric acid:



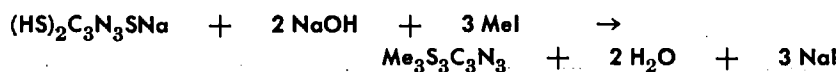
This ester is hydrolyzed in the presence of hydrochloric acid to methyl mercaptan and cyanuric acid:



This is evidence of its structure. The polymerization is aided by the presence of a little hydrochloric acid. Ethyl and isoamyl thiocyanates polymerize similarly. The esters are cleaved by sodium sulfide:

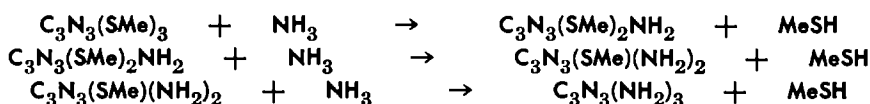


On partial acidification of the trisodium salt, an acid salt,  $(\text{HS})_2\text{C}_3\text{N}_3\text{SNa}$ , crystallizes out. The same salt, obtained from cyanuric chloride and sodium sulfide, can be methylated:



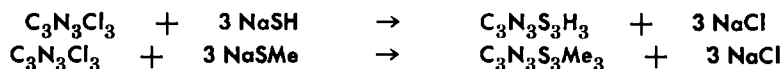
This ester is identical with the one from the polymerization of methyl thiocyanate. The free trithiocyanuric acid, which can be prepared by adding hydrochloric acid to the boiling solution of the sodium salt, is only slightly soluble in boiling water, insoluble in the usual solvents, and is stable up to  $200^\circ$ .

Ammonia, or an amine, displaces mercaptan from the ester progressively:



The final product is melamine.<sup>813, 814</sup>

The ester,  $\text{C}_3\text{N}_3(\text{SCH}_2\text{COOEt})_3$ , m.  $81^\circ$  was isolated from the residue after distilling the monomeric ethyl thiocyanofomate,  $\text{NCSCH}_2\text{COOEt}$ . Cyanuric chloride reacts with sodium hydrosulfide or mercaptide:



The trithiocyanuric acid and its methyl ester are identical with the same compounds made as described. The ethyl ester,  $\text{C}_3\text{N}_3(\text{SEt})_3$ , melts at  $27^\circ$  and boils at  $350^\circ$ . Oxidation of the

acid by iodine gives either  $(\text{CN})_3\text{S}_6(\text{CN})_3$  or  $\text{HO}(\text{CN})_3\text{S}_4(\text{CN})_3\text{OH}$  according to conditions.<sup>1018</sup>

Trithiocyanuric acid can be esterified by diazomethane or diazoethane.<sup>1363</sup>

Trithiocyanuric acid has been claimed as a brightening agent in plating with copper cyanide,<sup>752, 1275</sup> and as an accelerator in the vulcanization of rubber.<sup>1305b</sup> Certain N-substituted derivatives are said to have pharmaceutical value.<sup>149</sup> The reaction products of cyanuric chloride with dialkyl thiophosphates have been proposed as insecticides.<sup>427</sup>

### Kanarin

When dry chlorine, or bromine, reacts with the equivalent amount of potassium thiocyanate around  $150^\circ$ , a yellow solid is formed which has approximately the composition of thiocyanogen and is often called "pseudothiocyanogen." For best results, the amount of halogen should be equivalent to the base in the thiocyanate. When halogens, nitric acid, hydrogen peroxide, persulfates, or electrolytic oxygen act on concentrated aqueous solutions of salts of thiocyanic acid, more or less similar substances are produced. Their composition varies according to the method of preparation and they always contain some oxygen and hydrogen. By treating any of these products with alkali, a substance of the composition,  $\text{C}_8\text{H}_6\text{ON}_6\text{S}_7$ , called *Kanarin*, which dyes wool yellow, can be obtained.<sup>658g, 669, 671b, 683, 724, 786, 900, 1032, 1085, 1114, 1121, 1123a, 1123d, 1123g, 1132, 1193, 1246, 1372, 1384, 1421, 1445, 1446, 1577, 1830f</sup>

An early German patent, No. 1551<sup>1446</sup> by Procheroff describes the preparation of Kanarin.<sup>1577</sup> For dyeing, 100 g of it is dissolved in 1 liter of water with 100 g of borax.<sup>1032</sup>

A yellow dye from hydropseudothiocyanic acid may be related to Kanarin.<sup>1227</sup>

### Lists of Properties of Thiocyanic Esters and Isothiocyanates

The object of the following lists is to give the properties of a number of thiocyanates and isothiocyanates and—more important—to give references to the literature so that the method of preparing each compound may be ascertained. There is sometimes uncertainty whether a particular compound is a thiocyanate

or an isothiocyanate. Frequently the formulae are written RCNS and the structure has to be decided from the method of preparation. In some cases there is uncertainty as to isomerization of thiocyanates into isothiocyanates. When a compound has been prepared by several chemists, there are apt to be discrepancies between the values reported for the properties. This is due to the well-known carelessness of chemists in purifying and characterizing the compounds that they report.

#### ALKYL AND ARYL THIOCYANATES AND ISOTHIOCYANATES

The Raman spectra of thiocyanates and isothiocyanates have been studied, but few definite conclusions have been reached.<sup>393, 687, 938, 1060, 1362, 1398, 1767</sup> It is remarkable that the frequency 756 in phenyl isothiocyanate attributed to C=S does not differ appreciably from that of the C—S in the thiocyanates.<sup>1060, 1362</sup> The structure  $R-N^+ \equiv C-S^-$  has been advocated for the mustard oils.<sup>393</sup> Methyl thiocyanates shows the frequency characteristics of  $-C \equiv N$ .<sup>938</sup> From a consideration of the spectra of methyl and ethyl thiocyanates and isothiocyanates it has been concluded that there is no mesomerism of the SCN group.<sup>687</sup>

The absorption spectra of methyl and ethyl thiocyanates, and of methyl, ethyl, allyl, and phenyl isothiocyanates in methanol solution and in gas phase, indicate that they dissociate into  $R-SCN$  and  $R-NCS$ .<sup>1907</sup> In organic thiocyanates, the characteristic infrared absorption band is at a shorter wave length than in inorganic thiocyanates, indicating that the R is as  $RS-$ . The band positions for methyl thiocyanate are at 3.32 and 4.64 and for the isothiocyanate at 3.32 and 4.70. For the ethyl compounds, the comparable positions are 3.28 and 4.63, and 3.29 and 4.75.<sup>686</sup> The absorption of phenyl mustard oil in the 4.8  $\mu$  region has three components: 2130, 2080 and 1950  $cm^{-1}$ . The first two of these have counterparts in the Raman spectrum.<sup>1894</sup> An alkyl thiocyanate has a strong band at 1460  $\mu$  and the isothiocyanate additional bands at 1710 and 1515.<sup>1880</sup>

Despite all efforts at purification, the ultraviolet absorptions of alkyl thiocyanates and isothiocyanates are at the same wave number.<sup>1392</sup> The absorptions of mixtures of ethyl thiocyanate and hexane deviate from normal additive behavior.<sup>1393</sup>

The microwave spectra of methyl thiocyanate and isothio-



cyanate have been measured. There is good agreement between the theoretical and the observed spectra for  $\text{CH}_3\text{NCS}$ . The spectrum for  $\text{CH}_3\text{SCN}$  was found to be too weak for analysis.<sup>118</sup>

The alkyl thiocyanates and isothiocyanates have moderately large dielectric constants: 35.9 and 26.5 for methyl and ethyl thiocyanates, and 19.7 and 19.4 for the corresponding isothiocyanates. Tetraethylammonium iodide at volume 400 is dissociated in these four solvents 86, 77, 64, and 58% respectively.<sup>1847</sup> As a dissociating solvent, ethyl thiocyanate resembles ethyl iodide.<sup>187</sup> The molecular refractivity of tetraethylammonium iodide is 107.4 in methyl thiocyanate and only 99.2 in methanol.<sup>1847</sup>

The optical rotations of ethyl tartrate and malate are lower in thiocyanate and in isothiocyanate esters than in most other solvents.<sup>802</sup> There is a difference of  $11^\circ$  in the rotation of ethyl tartrate in ethyl thiocyanate and in isothiocyanate.<sup>1380</sup>

The dipole moments of halophenyl thiocyanates give  $127^\circ$  as the characteristic angle for  $-\text{SCN}$ <sup>144</sup> but show the  $-\text{NCS}$  group to be linear.<sup>145</sup>

The mean refractivity of the  $-\text{SCN}$  group is 23.2 whereas that of the  $-\text{NCS}$  is 28.1 in organic compounds, compared to 26.0 for inorganic.<sup>440, 441b, 441c</sup> The refractivity of sulfur in an alkyl thiocyanate is 7.91.<sup>1697</sup> The following values for  $M_D$  have been determined: <sup>6</sup>

MeNCS	20.98	EtNCS	26.22
MeNC	11.83	EtNC	16.50
Dif.	9.15		9.72

The surface energies of a number of alkyl thiocyanates and isothiocyanates have been measured.<sup>130</sup> From the parachors it is concluded that both  $-\text{SCN}$  and  $-\text{NCS}$  have linear structures<sup>1391</sup> and that the thiocyanate ion may be either  $\text{SCN}^-$  or  $\text{NCS}^-$ .<sup>1793</sup>

The molecular birefringence of ethyl isothiocyanate has been measured.<sup>376</sup> The specific heat of allyl mustard oil is 0.392 and its heat conductivity 0.0229.<sup>1858</sup> It gives no heat on mixing with pyrrole.<sup>431</sup> The ultrasonic velocity in phenyl isothiocyanate has been determined.<sup>1373</sup>

## COMPARISON OF ALKYL THIOCYANATES AND ISOTHIOCYANATES

The available data are so fragmentary that close comparisons cannot be made. Except for the methyl and ethyl compounds, the densities are mostly at odd temperatures. The information on refractivity is scanty. Indexes for the thiocyanates are slightly above 1.46, and for the isothiocyanates around 1.51. For the two ethyl compounds the difference is 0.0489. The densities of other pairs of isomers are nearly the same.

In Table 1.3 are given the boiling points of the alkyl thiocyanates and isothiocyanates from methyl to butyl, and of the normal alcohols and alkanes of approximately the same molecular weights. As is usual, the methyl compounds boil relatively high. The boiling points of the isothiocyanates are lower than those of the thiocyanates and are remarkably close to those of the alcohols of approximately the same molecular weights. Comparison of the boiling points with those of the alkanes indicates that the alkyl thiocyanates and isothiocyanates, like the alcohols, are highly associated.

The melting points of the methyl and ethyl isothiocyanates are  $35.9^\circ$  and  $-5.9^\circ$ , which are much higher than those of the corresponding thiocyanates-  $-54.5^\circ$  and  $-85.5^\circ$ .

The methyl isothiocyanate is the only one of either series, below octadecyl, which is a solid at room temperature.

Data for a larger number of compounds are given in subsequent tables.

TABLE 1.3  
*Boiling Points of Alkyl Thiocyanate Derivatives*

	<i>Me</i>	<i>Et</i>	<i>Pr</i>	<i>Bu</i>
RSCN	$133^\circ\text{C}$	$146^\circ\text{C}$	$164^\circ\text{C}$	$186^\circ\text{C}$
RNCS	$119^\circ$	$134^\circ$	$153^\circ$	$167^\circ$
RBu	$36^\circ$	$69^\circ$	$98.4^\circ$	$126^\circ$
$\text{R}(\text{CH}_2)_3\text{OH}$	$118^\circ$	$138^\circ$	$158^\circ$	$175^\circ$

## Properties of Thiocyanates

## ALKYL THIOCYANATES

Methyl,  $\text{CH}_3\text{SCN}$ , m.  $-54.5^\circ$ ,<sup>1783</sup>  $-53.58^\circ$ ,<sup>647a</sup>  $-51^\circ$ ,<sup>1847</sup>  $b_{760}$   
 $130-2^\circ$ ,<sup>1498</sup>  $b_{758}$   $130.50^\circ$ ,<sup>647a</sup>  $130-1^\circ$ ,<sup>765</sup>  $b_{757}$   $130.2-0.4^\circ$ ,<sup>850</sup>

130.5°, <sup>1678, 1847</sup> 130.4°, <sup>1358</sup> 133.9°, <sup>1847</sup> 132.9°, <sup>937, 1409</sup> 130°, <sup>549</sup> 128°, <sup>956</sup> b<sub>756</sub> 130.50°, b<sub>755</sub> 129.5°, <sup>1847</sup> b<sub>749</sub> 129.6–30, <sup>1301</sup> 133°, <sup>813, 814, 1506, 1847</sup> 132°, 132–3°, <sup>288a</sup> b<sub>762</sub> 131°, <sup>647a, 647b, 647c</sup> b<sub>770</sub> 130°, <sup>150a, 150b, 150c</sup> b<sub>777</sub> 131.45°, <sup>647a</sup> b. 131°, <sup>240</sup> 130–33°, <sup>1363</sup> d 0/4 1.0958, <sup>1847</sup> 1.0970, <sup>1847</sup> d 15/4 1.0765, <sup>412d</sup> d 16/4 1.0778, <sup>765</sup> d 18/4 1.0765, <sup>412d</sup> d 20/4 1.0750, <sup>850</sup> 1.0759, <sup>1721</sup> d 20/20 1.0730, d 23.8/4 1.06935, <sup>412d, 1301</sup> d 25/4 1.0675, <sup>1847</sup> 1.06782, <sup>1847</sup> 1.0691, <sup>850</sup> 1.0672, <sup>1847</sup> d 38.2/4, 1.0675, <sup>1391</sup> d 50/4 1.0380, <sup>1847</sup> d 55/4 1.0331, d 70/4 1.0149, <sup>765</sup> d<sub>0</sub> 1.08794, <sup>1409</sup> d<sub>t</sub> 1.0958 (1.001055t); <sup>1847</sup> n 12.5/D 1.4764, <sup>765</sup> n 15/D 1.4745, <sup>412d</sup> n 20/D 1.4582, <sup>647a</sup> 1.4680, <sup>1721</sup> 1.4697, <sup>850</sup> 1.0730, n 23.8/D 1.46801, <sup>412d, 1301</sup> n 25/D 1.46694, <sup>1847</sup> n 40/D 1.4582, <sup>647a</sup> n 29/D 1.4670, n 48/D 1.4562, n 59/D 1.4450, n 76/D 1.4410; <sup>765</sup> Molecular heat of combustion (gas) at constant volume 452.1 cal; at constant pressure 453.1 cal; <sup>150a, 150b, 150c</sup> (liquid) at constant pressure 398.95 cal; <sup>1775</sup> molecular boiling point rise 26.4°; <sup>1847</sup> heat of formation –19.9 cal; <sup>150b</sup> heat of fusion 2057 cal; <sup>647a</sup> dielectric constant 35.9 at 20°, <sup>1847</sup> 33.3 at 15.5°, <sup>486, 937</sup> 35.5 at 12°; <sup>1209</sup> specific conductivity  $3.7 \times 10^{-5}$ ,  $0.146 \times 10^{-5}$ ; <sup>1207</sup> association factor 1.51, <sup>1847</sup> at b.p. 1.26; <sup>1847</sup> parachor 170.2. <sup>1391</sup>

Ethyl, CH<sub>3</sub>CH<sub>2</sub>SCN, m. –85.5°; <sup>1783</sup> b<sub>37</sub> 56°, <sup>150b</sup> b<sub>780</sub> 144.4°, <sup>1434, 1783</sup> 144–6°, <sup>1498</sup> 146.2°, <sup>850</sup> b<sub>758</sub> 145.2–5.4°, <sup>765</sup> b<sub>752</sub> 143–4°, <sup>1847</sup> b<sub>749</sub> 143.6°, <sup>1301</sup> b<sub>738</sub> 141.5–3.0°, <sup>937</sup> b<sub>765</sub> 145°, <sup>1847</sup> b. 143.5°, <sup>1847</sup> 141–2°, <sup>1158, 1240</sup> 142–3°, <sup>1166</sup> 140–1°, <sup>224</sup> 140–2°, <sup>1363</sup> 148°, <sup>367</sup> 142.5°, <sup>486</sup> 146°, <sup>111, 268a, 286a</sup> 145°, <sup>802</sup> 143°, <sup>150b, 1207</sup> d 0/4 1.0232, <sup>1847</sup> 1.0209, <sup>1847</sup> d<sub>0</sub> 1.0330, <sup>268a</sup> d<sub>12</sub> 1.021, <sup>1847</sup> d 15/4 1.0150, <sup>765</sup> d<sub>16</sub> 1.020, <sup>286</sup> d<sub>17.6</sub> 1.013, <sup>1468</sup> d<sub>19</sub> 1.0126, <sup>268a</sup> d<sub>20</sub> 1.0099, <sup>655</sup> d 20/4 1.0084, <sup>1721</sup> 1.0106, d 20/20 1.005, d 22.9/4 1.00715, <sup>412d, 1301</sup> d<sub>23</sub> 1.00238, <sup>268a</sup> d 25/4 0.9976, <sup>1847</sup> 0.9964 vac., <sup>1847</sup> 1.0051, <sup>850</sup> d 40/4 0.9885, <sup>765</sup> d<sub>46.4</sub> 0.981, <sup>1468</sup> d 71/4 0.9557, d 78/4 0.9491, <sup>765</sup> d 78.4 0.945, <sup>1468</sup> d<sub>146</sub> 0.870135, 0.8698; <sup>268a</sup> n 15/D 1.4684, <sup>765</sup> n 18/D 1.4732, <sup>655</sup> n 20/D 1.4641, <sup>850</sup> 1.4670, 1.4653, <sup>802</sup> 1.4616, <sup>1721</sup> n 22.9/D 1.46533, <sup>412d, 1301</sup> n 29/D 1.4612, <sup>765</sup> n 49/D 1.4512, n 60/D 1.4447, n 64/D 1.4430, n 75.4/D 1.4368, n 78/D 1.4353; <sup>765</sup> surface tension at 17.6° 35.32, at 46.4° 31.79, at 78/4° 27.99; <sup>1468</sup> surface energy 72.3; <sup>748</sup> heat of formation –17.25 cal; <sup>150b</sup> molecular heat of combustion at constant volume 612.5 cal; at constant pressure 613.8 cal; <sup>150</sup> dielectric constant 34.6 at 2.5°, 29.3 at 21°, <sup>1847</sup> 31.2 at 11.5°, <sup>937</sup> 31.0 at 12°, <sup>1207</sup> 26.5 at 20°; <sup>1847</sup> specific conductivity,  $2.16 \times 10^{-5}$ ,

- $0.26 \times 10^{-5}$ ; <sup>1207</sup> association factor 1.17, <sup>1847</sup> at b.p.  $1.14^\circ$ ; <sup>1847</sup> critical temp.  $381.1^\circ$ . <sup>1468</sup>
- n*-Propyl,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{SCN}_2$ ,  $b_{760}$   $163-5^\circ$ , <sup>1498</sup> b.  $164^\circ$ , <sup>1878</sup>  $163^\circ$ , <sup>1579</sup>, <sup>224</sup>
- i*-Propyl,  $\text{Me}_2\text{CHSCN}$ ,  $b_{760}$   $151-2^\circ$ , <sup>1498</sup>  $b_{754}$   $152-3^\circ$ ; <sup>637</sup>  $d_{20}$  0.963. <sup>779a</sup>
- n*-Butyl,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SCN}$ ,  $b_{760}$   $185.5-7.0^\circ$ , <sup>1498</sup>  $b_{748}$   $184.5-5.5^\circ$ , <sup>984</sup> b.  $173-5^\circ$ ; <sup>224</sup>  $d$  25/4 0.9563;  $n$  21.5/D 1.4636. <sup>984</sup>
- i*-Butyl,  $\text{Me}_2\text{CHCH}_2\text{SCN}$ , m.  $-59.0^\circ$ ;  $b_{760}$   $175.4^\circ$ , <sup>1873</sup>  $b_{15}$   $66^\circ$ , <sup>1498</sup> b.  $174-6^\circ$ . <sup>817</sup>
- s*-Butyl,  $\text{CH}_3\text{CH}_2\text{CHMeSCN}$ ,  $b_7$   $48.5-9.5^\circ$ ; <sup>1128</sup>  $d$  22/4 0.960;  $n$  19.5/D 1.4621;  $[\alpha]$  22/5893  $-44.64^\circ$ ,  $[\alpha]$  22/4359  $-74.80^\circ$ . <sup>991</sup>
- t*-Butyl,  $\text{Me}_3\text{CSCN}$ ,  $b_{10}$   $39-40^\circ$ . <sup>1584</sup>
- n*-Amyl,  $\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{SCN}$ ,  $b_{12}$   $89^\circ$ , <sup>1721</sup>  $b_{13-4}$   $8608^\circ$ , <sup>1498</sup>  $b_{16}$   $90-1^\circ$ ; <sup>21</sup>  $d$  20/4 0.9486, <sup>1721</sup>  $d$  25/4 0.9412; <sup>21</sup>  $n$  20/D 1.4636, <sup>1721</sup>  $n$  25/D 1.4670. <sup>21</sup>
- i*-Amyl,  $\text{Me}_2\text{CHCH}_2\text{CH}_2\text{SCN}$ ,  $b_{16}$   $84-5^\circ$ , <sup>1498</sup>  $b_{739}$   $193.5-5.0^\circ$ , <sup>937</sup> b.  $197^\circ$ ; <sup>1220</sup>  $d_{20}$  0.905; <sup>781</sup> dielectric constant 17.1 at  $19.5^\circ$ . <sup>486</sup>, <sup>937</sup>
- c*-Pentyl,  $(\text{CH}_2\text{CH}_2)_2\text{CH}_2\text{SCN}$ ,  $b_{17}$   $96-7^\circ$ . <sup>1498</sup>
- n*-Hexyl,  $\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{SCN}$ ,  $b_2$   $86-8^\circ$ , <sup>1498</sup>  $b_{18}$   $108-9^\circ$ , <sup>1879</sup> b.  $215-20^\circ$ ;  $d_{20}$  0.922. <sup>1386</sup>
- s*-Hexyl,  $\text{CH}_3(\text{CH}_2)_5\text{CHMeSCN}$ , b.  $209-10.5^\circ$ . <sup>1813</sup>
- c*-Hexyl,  $\text{CH}_2(\text{CH}_2\text{CH}_2)_2\text{CH}_2\text{SCN}$ ,  $b_9$   $94-5^\circ$ ,  $b_{10}$   $103-4^\circ$ , <sup>1498</sup>  $b_{13}$   $111.5^\circ$ , <sup>1721</sup>  $b_{16}$   $111-2^\circ$ ;  $d$  25/4 1.0402, <sup>21</sup>  $d$  20/4 1.0460; <sup>1721</sup>  $n$  20/D 1.5060, <sup>1721</sup>  $n$  25/D 1.5055. <sup>21</sup>
- 3-Thiocyanohexane,  $\text{PrCH}(\text{SCN})\text{Et}$ ,  $b_{40}$   $120^\circ$ ;  $d$  20/4 0.930;  $n$  20/D 1.5608. <sup>1697</sup>
- n*-Heptyl,  $\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{SCN}$ ,  $b_9$   $106-7^\circ$ , <sup>1498</sup>  $b_{28}$   $136^\circ$ , b.  $234-6^\circ$ ; <sup>193</sup>  $d_{20}$  0.92. <sup>193</sup>
- n*-Octyl,  $\text{CH}_3(\text{CH}_2)_7\text{CH}_2\text{SCN}$ ,  $b_{0.15}$   $83.5-3.5^\circ$ , <sup>1498</sup>  $b_{11}$   $122-4^\circ$ , <sup>452</sup>  $b_{19}$   $141-2^\circ$ ;  $d$  25/4 0.9149;  $n$  25/D 1.4642, <sup>21</sup>  $n$  20/D 1.4649. <sup>452</sup>
- s*-Octyl,  $\text{CH}_3(\text{CH}_2)_7\text{CHMeSCN}$ , b.  $142^\circ$ , <sup>897a</sup>, <sup>b</sup>  $b_4$   $98.5-9^\circ$ , <sup>1510</sup>  $b_{15}$   $119-20^\circ$ ; <sup>991</sup>  $d$  20/4 0.919, <sup>1510</sup> 0.914; <sup>886</sup>  $n$  17/D 1.4651, <sup>991</sup>  $n$  20/D 1.4635;  $[\alpha]$  20/D  $51.7^\circ$ , <sup>1510</sup>  $[\alpha]$  20/5893  $62.0^\circ$ ,  $[\alpha]$  20/5461  $74.9^\circ$ ,  $[\alpha]$  20/4358  $121.5^\circ$ . <sup>886</sup>
- n*-Nonyl,  $\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{SCN}$ ,  $b_{0.1}$   $92-4^\circ$ . <sup>1498</sup>
- 1-Methyloctyl,  $\text{CH}_3(\text{CH}_2)_8\text{CHMeSCN}$ , b.  $142^\circ$ . <sup>781</sup>
- 3,5,5-Trimethylhexyl,  $\text{Me}_3\text{CCH}_2\text{CHMeCH}_2\text{CH}_2\text{SCN}$ ,  $b_{12}$   $122^\circ$ ; <sup>257</sup>  $n$  25/D 1.4638. <sup>257</sup>
- n*-Decyl,  $\text{CH}_3(\text{CH}_2)_9\text{CH}_2\text{SCN}$ ,  $b_{0.3}$   $107-8^\circ$ , <sup>1498</sup>  $b_{15}$   $154-5^\circ$ , <sup>21</sup>  $b_{11}$

- 158°; d 20/4 0.9063,<sup>1721</sup> d 25/4 0.9047; n 25/D 1.4652,<sup>21</sup> n 20/D 1.4658.<sup>1721</sup>
- n*-Undecyl,  $\text{CH}_3(\text{CH}_2)_9\text{CH}_2\text{SCN}$ ,  $b_{0.4}$  124–5°, <sup>1498</sup>  $b_{0.1}$  140–50°, <sup>1842</sup>  $b_{10}$  160–1°; d 25/4 0.9007; n 25/D 1.4653,<sup>21</sup> n 20.5/D 1.4661.<sup>1842</sup>
- n*-Dodecyl, lauryl,  $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{SCN}$ ,  $b_{0.2}$  128–9°, <sup>1498</sup>  $b_{0.55}$  137°, <sup>1721</sup>  $b_2$  155–6°, <sup>1741</sup>  $b_{2.5}$  154–6°, <sup>690</sup>  $b_{10}$  170–2°; d 25/4 0.8958,<sup>21</sup> d 20/4 0.8997; n 20/D 1.4660,<sup>1721</sup> n 25/D 1.4657.<sup>21</sup>
- n*-Tridecyl,  $\text{CH}_3(\text{CH}_2)_{11}\text{CH}_2\text{SCN}$ ,  $b_7$  173–6°; d 25/4 0.8935; n 25/D 1.4661.<sup>21</sup>
- n*-Tetradecyl, myristyl,  $\text{CH}_3(\text{CH}_2)_{12}\text{CH}_2\text{SCN}$ ,  $b_{0.1}$  145.5–7.5°. <sup>1498</sup>
- n*-Pentadecyl,  $\text{CH}_3(\text{CH}_2)_{13}\text{CH}_2\text{SCN}$ ,  $b_{0.1}$  154–6°. <sup>1498</sup>
- Cetyl,  $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{SCN}$ , m. 15.5°; <sup>1878</sup>  $b_{0.1}$  163–6°; <sup>1498</sup>  $b_{0.2}$  190–5°, <sup>1842</sup>  $b_{13}$  222–7°, <sup>1878</sup>  $b_{30}$  242–9°. <sup>1878</sup>
- n*-Octadecyl,  $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{SCN}$ , m. 27°. <sup>578</sup>
- Dihydrohydnocarpyl,  $\text{C}_5\text{H}_9(\text{CH}_2)_{10}\text{CH}_2\text{SCN}$ ,  $b_{0.3}$  205–15°; n 21/D 1.4840. <sup>1842</sup>
- 7-Dihydrocholesteryl, m. 130–6°. <sup>1405</sup>
- 2-Thiocyanobutadiene,  $\text{CH}_2:\text{CH}\cdot\text{C}(\text{SCN}):\text{CH}_2$ ,  $b_{27}$  69–72°; d 20/4 1.048; n 20/D 1.518. <sup>1048</sup>
- Oleyl,  $\text{C}_{17}\text{H}_{33}\text{CH}_2\text{SCN}$ ,  $b_{0.1}$  205–10°; <sup>1104.5</sup> n 20/D 1.4211. <sup>1104.5, 1842</sup>
- Elaidyl (*trans*),  $\text{C}_{17}\text{H}_{33}\text{CH}_2\text{SCN}$ ,  $b_{0.1}$  198–9°; n 20/D 1.4749. <sup>1842</sup>
- Linolyl,  $\text{C}_{17}\text{H}_{31}\text{CH}_2\text{SCN}$ ,  $b_{0.15}$  202°; n 18.5/D 1.4931. <sup>1842</sup>
- Hydnocarpyl,  $\text{C}_5\text{H}_7(\text{CH}_2)_{10}\text{CH}_2\text{SCN}$ ,  $b_{0.5}$  190–210°; n 21/d 1.4840. <sup>1842</sup>
- Cholesteryl, m. 130°, <sup>1842</sup> 129°, <sup>635</sup> 128°, <sup>1280</sup> 126–8°; <sup>1329.5</sup>  $[\alpha]_D$  –10.97°, <sup>635, 1842</sup>  $[\alpha]_D$  –10°, <sup>1329.5</sup>  $[\alpha]$  19/D –14.6°. <sup>684, 1280, 1830a, d, e</sup>
- 3- $\alpha$ -Thiocyano-5-cholestene, m. 120°. <sup>210.5</sup>

## SUBSTITUTED ALKYL THIOCYANATES

*Halothiocyanates*

- $\text{FCH}_2\text{CH}_2\text{SCN}$ ,  $b_{19}$  77.5–8.5°, <sup>1558</sup>  $b_{20}$  78–9°; n 25/D 1.4615. <sup>841</sup>
- $\text{FCH}_2\text{CH}_2\text{CH}_2\text{SCN}$ ,  $b_{10}$  78–9°; n 25/D 1.4591. <sup>841</sup>
- $\text{FCH}_2(\text{CH}_2)_3\text{SCN}$ ,  $b_{13}$  97–8°; n 25/D 1.4610. <sup>841</sup>
- $\text{FCH}_2(\text{CH}_2)_4\text{CH}_2\text{SCN}$ ,  $b_{11}$  112–3°; n 25/D 1.4603. <sup>841</sup>
- $\text{F}_3\text{C}(\text{CH}_2)_3\text{CH}_2\text{SCN}$ ,  $b_8$  82°. <sup>1552b</sup>
- $\text{ClCH}_2\text{SCN}$ ,  $b_{40}$  95°,  $b$  185°;  $d_{15}$  1.37. <sup>417</sup>
- $\text{Cl}_3\text{CSCN}$ , m. 2.5°;  $b_{11}$  44.5°, <sup>1342.5</sup>  $b_{16}$  55°,  $b_{50}$  79°, <sup>242</sup>  $b_{741}$

- 164.5°;<sup>1342.5</sup>  $d_{20}$  1.585;<sup>242</sup>  $n_{20/D}$  1.5222; specific heat at 39° 0.262.<sup>1342.5</sup>
- $\text{ClCH}_2\text{CH}_2\text{SCN}$ ,  $b_{15}$  93°;<sup>1379</sup>  $b_{15}$  91–2°;<sup>1049</sup>  $b_{20}$  99–100°;<sup>37</sup>  $b_{25}$  106°;<sup>415</sup>  $b_{768}$  198–202°;<sup>37</sup>  $b.$  202–3°;<sup>860</sup>  $d_{15}$  1.298;<sup>415</sup>  $d_{20/4}$  1.3037;<sup>1721</sup>  $d_{23/4}$  1.283;<sup>37</sup>  $n_{20/D}$  1.5158;<sup>1721</sup>  $n_{23/D}$  1.5100.<sup>37</sup>
- $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{SCN}$ ,  $b_{12}$  115°;<sup>1379</sup>  $b.$  222–3°;  $d_{19.5}$  1.226.<sup>779g</sup>
- $\text{ClCH}_2\text{CHMeCH}_2\text{SCN}$ ,  $b_1$  77°;  $n_{20/D}$  1.4994.<sup>55.5</sup>
- $\text{ClCH}_2(\text{CH}_2)_2\text{CH}_2\text{SCN}$ ,  $b_{1.5}$  88.5–90.5°;<sup>7</sup>  $b_{12}$  134°;<sup>1379</sup>  $n_{20/D}$  1.5023.<sup>7</sup>
- $\text{Cl}_3\text{CCH}_2(\text{CH}_2)_2\text{CH}_2\text{SCN}$ ,  $b_2$  136–7°.<sup>1552b</sup>
- $\text{ClCH}_2(\text{CH}_2)_3\text{CH}_2\text{SCN}$ ,  $b_{10}$  144–5°.<sup>1379</sup>
- $\text{Cl}_3\text{CCH}_2(\text{CH}_2)_4\text{CH}_2\text{SCN}$ ,  $b_3$  153–5°.<sup>1552b</sup>
- $\text{Cl}_3\text{CCH}_2(\text{CH}_2)_6\text{CH}_2\text{SCN}$ ,  $b_3$  161–4°.<sup>1552b</sup>
- $\text{ClCH}:\text{CHCH}_2\text{SCN}$ ,  $b_{0.2}$  72–8°.<sup>342</sup>
- $\text{ClCMe}:\text{CHCH}_2\text{SCN}$ ,  $b_{16}$  100–5°;<sup>1444</sup>  $b_{25}$  107–9°;  $d_{15/4}$  1.1852;  $n_{15/D}$  1.5608.<sup>1695</sup>
- 2-Chlorocyclohexylthiocyanate,  $b_{0.1}$  90–2°;<sup>529</sup>  $b_{21}$  154–6°;<sup>37</sup>  $n_{14/D}$  1.5308.<sup>37</sup>
- 2-Chlorocyclohexyldichlorothiocyanate,  $b_{0.1}$  80–2°;<sup>77</sup>  $n_{25/D}$  1.5620.<sup>77</sup>
- $\text{ClCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}(\text{CH}_2)_4\text{SCN}$ ,  $b_{0.1}$  146–8°;  $n_{18/D}$  1.4970.<sup>334.5</sup>
- $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{SCN}$ ,  $b_{1.5}$  72°;<sup>9</sup>  $n_{20/D}$  1.5350.<sup>9</sup>
- $\text{BrCHMeCHMeSCN}$ ,  $b_{10}$  105°.<sup>1128</sup>
- $\text{BrCHEtCHMeSCN}$ ,  $b_{10}$  110–18°.<sup>1128</sup>
- $\text{BrCH}_2(\text{CH}_2)_2\text{CH}_2\text{SCN}$ ,  $n_{20/D}$  1.5288.<sup>7</sup>
- 7-Bromocholesteryl,  $m.$  108–11°.<sup>1405</sup>

### Hydroxy Thiocyanates

- $\text{HOCH}_2\text{CH}_2\text{SCN}$ ,  $b_{0.012}$  104–7°;<sup>1637</sup>  $b_{0.3}$  121–3°;<sup>1841b</sup>  $b_{2-3}$  112–3°;<sup>1824</sup>  $b_{21}$  151° (dec);  $d_{20/4}$  1.2258;  $n_{20/D}$  1.514;<sup>1637</sup> 1.5118;<sup>1824</sup> Esters: Ac,  $n_{20/D}$  1.4750;<sup>1824</sup> Maleate, diester,  $m.$  80°;<sup>1637</sup> Nicotinate,  $m.$  77°;<sup>1824</sup>  $\text{RNHCO}_2(\text{CH}_2)_2\text{SCN}$ ,  $R=\text{Ph}$ ,  $m.$  59°;<sup>1746</sup>  $p\text{-O}_2\text{NC}_6\text{H}_4$ ,  $m.$  83°.<sup>1746</sup>  $p\text{-MeOC}_6\text{H}_4$ ,  $m.$  70°;<sup>1746</sup>  $\text{MeC}_6\text{H}_4$ ,  $o$ ,  $m.$  40–2°;<sup>1746</sup>  $p$ ,  $m.$  57°.<sup>1746</sup>
- $\text{HOCH}_2\text{CHMeSCN}$ ,  $b_{0.1}$  107°;<sup>1831</sup>  $b_1$  120–2°;  $n_{20/D}$  1.5059;<sup>1824</sup>  $n_{21.5/D}$  1.5048;<sup>998, 1831</sup> Nicotinate,  $b_{0.5}$  143°;<sup>1824</sup>  $b_{0.9}$  146°;  $n_{20/D}$  1.5470; picrate,  $m.$  104°.<sup>1824</sup>
- $\text{HOCHMeCH}_2\text{SCN}$ ,  $b_{0.2}$  98–100°;  $n_{25/D}$  1.4976.<sup>1438.5</sup>
- $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{SCN}$ ,  $b_4$  114°;<sup>1925.5</sup>  $b_{0.3}$  93°;  $n_{20/D}$  1.4981;<sup>1824</sup>

- Nicotinate, m.  $44^{\circ}$ ;  $b_{0.2}$   $182-4^{\circ}$ ; n 20/D 1.5488; picrate, m.  $79^{\circ}$ .<sup>1824</sup>
- $\text{HOCH}_2(\text{CH}_2)_2\text{CH}_2\text{SCN}$ ,  $b_1$   $128-9^{\circ}$ ; n 20/D 1.5004; <sup>1824</sup> Ac,  $b_{1.35-1.40}$   $112-4^{\circ}$ , <sup>1623b</sup>  $b_6$   $130-2^{\circ}$ ; d 22/4 1.1089; <sup>1737</sup> n 0/D 1.474, <sup>1737</sup> n 25/D 1.4727; <sup>1623b</sup> Propionate,  $b_{0.25}$   $103.8^{\circ}$ ; n 25/D 1.4710; <sup>1623b</sup> Nicotinate,  $b_{0.8}$   $90^{\circ}$ ; n 20/D 1.5431; picrate, m.  $75^{\circ}$ .<sup>1824</sup>
- $\text{HOCH}_2(\text{CH}_2)_3\text{CH}_2\text{SCN}$ ,  $b_{0.2}$   $124-5^{\circ}$ ; n 20/D 1.4958; <sup>1824</sup> Ac,  $b_{0.4}$   $102^{\circ}$ ; n 25/D 1.4710; Propionate,  $b_{0.5}$   $114.8-115^{\circ}$ ; n 25/D 1.4701; <sup>1623b</sup> Nicotinate, n 20/D 1.5426; picrate, m.  $181^{\circ}$ .<sup>1824</sup>
- $\text{HOCHMeCH}_2\text{CHMeSCN}$ ,  $b_6$   $112^{\circ}$ .<sup>1925.5</sup>
- $\text{HOCH}_2(\text{CH}_2)_4\text{CH}_2\text{SCN}$ ,  $b_1$   $135-6^{\circ}$ ,<sup>1824</sup>  $b_{3-4}$   $157^{\circ}$ ; <sup>1823.5</sup> n 20/D 1.4933.<sup>1824</sup>
- 2-Hydroxycyclohexylthiocyanate,  $b_7$   $148-50^{\circ}$ ; n 25/D 1.5307.<sup>1822</sup>
- $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SCN}$ ,  $b_{0.5}$   $104-5^{\circ}$ ; d 25/4 1.1855; n 25/D 1.4965.<sup>258.5</sup>
- $\text{HOCH}_2\text{CH}_2\text{OCH}_2(\text{CH}_2)_4\text{CH}_2\text{SCN}$ ,  $b_{0.15}$   $163-6^{\circ}$ ; n 20/D 1.4955.<sup>334.5</sup>
- $\text{HOCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}(\text{CH}_2)_6\text{SCN}$ ,  $b_{0.1}$   $181-6^{\circ}$ ; n 21.5/D 1.5075.<sup>334.5</sup>
- Acetothiocyano-glucose, m.  $111.5-3^{\circ}$ .<sup>543b</sup>
- Tetraacetyl-1-thiocyano- $\beta$ -glucose, m.  $132^{\circ}$ ;  $[\alpha]_D$   $-21.8^{\circ}$ .<sup>1889</sup>
- Thiocyanoglucose-6-bromohydrin, triAc, m.  $164.5^{\circ}$ .<sup>544</sup>
- Triacetyl-6-thiocyano- $\beta$ -methylglucoside, m.  $135^{\circ}$ .<sup>1899</sup>
- Aceto-thiocyanatocellobiose, m.  $201^{\circ}$ ;  $[\alpha]$  19/D  $-7.48^{\circ}$ .<sup>172</sup>
- 7-Thiocyanochloesterol, m.  $140^{\circ}$ ;  $[\alpha]$  20/D  $-350^{\circ}$ ; Bz., m.  $165^{\circ}$ ;  $[\alpha]$  20/D  $-224^{\circ}$ .<sup>566</sup>
- 3- $\alpha$ -Thiocyano-6- $\beta$ -hydroxy-5- $\alpha$ -cholestane, m.  $136^{\circ}$ .<sup>210.5</sup>

### Ether Thiocyanates

- $\text{PhOCH}_2\text{SCN}$ ,  $b_{20}$   $124-5^{\circ}$ .<sup>96</sup>
- $\text{ClC}_6\text{H}_4\text{OCH}_2\text{SCN}$ , *o*-, m.  $1-2^{\circ}$ ;  $b_{0.05}$   $116-7^{\circ}$ ; *m*-, m.  $-7$  to  $-6^{\circ}$ ;  $b_{0.2}$   $108-9^{\circ}$ ; *p*-, m.  $42^{\circ}$ ,<sup>96</sup>  $40-2^{\circ}$ ; <sup>1214</sup>  $b_{0.4}$   $105-6^{\circ}$ .<sup>96</sup>
- $\text{Cl}_2\text{C}_6\text{H}_3\text{OCH}_2\text{SCN}$ , 2,4-, m.  $44^{\circ}$ ; <sup>96, 96.5, 1214</sup> 2,5-, m.  $61^{\circ}$ ; <sup>96, 1214</sup> 3,4-, m.  $75^{\circ}$ .<sup>96, 1214</sup>
- p*- $\text{BrC}_6\text{H}_4\text{OCH}_2\text{SCN}$ , m.  $54-6^{\circ}$ .<sup>96</sup>
- p*- $\text{NO}_2\text{C}_6\text{H}_4\text{OCH}_2\text{SCN}$ , m.  $66-8^{\circ}$ .<sup>96</sup>
- 2,4- $\text{O}_2\text{N}(\text{Cl})\text{C}_6\text{H}_3\text{OCH}_2\text{SCN}$ , m.  $91^{\circ}$ .<sup>96</sup>
- p*- $\text{MeOC}_6\text{H}_4\text{OCH}_2\text{SCN}$ ,  $b_{0.3}$   $112-4^{\circ}$ .<sup>96</sup>

- $p$ -MeC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>SCN, m. 1–2°; b<sub>20</sub> 150–2°.<sup>96</sup>  
 ClMeC<sub>6</sub>H<sub>3</sub>OCH<sub>2</sub>SCN, 3,4-, m. 33°;<sup>96</sup> 4,2-, m. 40°; 4,3-, m. 33°.<sup>96</sup>  
 4,3,5-ClMe<sub>2</sub>C<sub>6</sub>H<sub>2</sub>OCH<sub>2</sub>SCN, m. 78°.<sup>96</sup>  
 $\alpha$ -C<sub>10</sub>H<sub>7</sub>OCH<sub>2</sub>SCN, m. 40°; b<sub>0.15</sub> 139–40°.<sup>96</sup>  
 EtOCH<sub>2</sub>CH<sub>2</sub>SCN, d 20/4 1.04291 n 20/D 1.4608.<sup>1721</sup>  
 BuOCH<sub>2</sub>CH<sub>2</sub>SCN, d 20/4 0.9991; n 20/D 1.4628.<sup>1721</sup>  
 PhOCH<sub>2</sub>CH<sub>2</sub>SCN, b<sub>0.4</sub> 152°;<sup>633</sup> b<sub>5</sub> 157–9°;<sup>1274.5</sup> n 20/D 1.5579,<sup>1274.5</sup> 1.5599,<sup>633</sup> n 25/D 1.5579.<sup>1746</sup>  
 ClC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>2</sub>SCN, *o*-, m. 37–9°; b<sub>3.0</sub> 180°; *m*-, b<sub>0.1</sub> 126°; *p*-, b<sub>0.1</sub> 137°; b<sub>3</sub> 153–5°;<sup>633</sup> n 20/D 1.5710.<sup>633</sup>  
 2,4,6-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>SCN, b<sub>3</sub> 185–6°.<sup>361</sup>  
 BrC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>2</sub>SCN, *o*-, b<sub>1.7</sub> 162°; n 20/D 1.5920;<sup>633</sup> *p*-, m. 63°;<sup>633</sup> b<sub>3</sub> 181–2°.<sup>633</sup>  
 $p$ -MeOC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>2</sub>SCN, b<sub>0.4</sub> 140°;<sup>633</sup> 141°.<sup>633</sup>  
 MeC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>2</sub>SCN, *o*-, b<sub>0.3</sub> 132°;<sup>633</sup> *m*-, b<sub>4.0</sub> 158°; n 20/D 1.5534; *p*-, b<sub>0.5</sub> 130°; n 20/D 1.5530.<sup>633</sup>  
 $o$ -Me<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>2</sub>SCN, b<sub>0.3</sub> 123°; n 20/D 1.5402.<sup>633</sup>  
 $p$ -Me<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>2</sub>SCN, b<sub>2.5</sub> 158–63°.<sup>362</sup>  
 $c$ -HexC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>2</sub>SCN, *o*-, b<sub>3</sub> 174–8°.<sup>1133</sup>  
 3,4-Me<sub>2</sub>C:C<sub>6</sub>H<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>SCN, b<sub>0.3</sub> 130°.<sup>633</sup>  
 $o$ -ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>SCN, b<sub>1.5</sub> 160; n 20/D 1.5528.<sup>633</sup>  
 $p$ -O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>SCN, m. 59°.<sup>1065</sup>  
 PhOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>SCN b<sub>2</sub> 163–3.5°.<sup>363b</sup>  
 $p$ -O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>OCHMeCH<sub>2</sub>SCN, m. 43°.<sup>1065</sup>  
 PhOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCN, b<sub>0.4</sub> 125°; n 20/D 1.5518.<sup>633</sup>  
 ClC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCN, *o*-, b<sub>1.3</sub> 165°; n 20/D 1.5644;<sup>633</sup> *m*-, b<sub>1.2</sub> 164°; n 20/D 1.5624; *p*-, b<sub>0.5</sub> 50°.<sup>633</sup>  
 2,4,6-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCN, b<sub>4</sub> 195–6°.<sup>361</sup>  
 $p$ -BrC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCN, m. 49°;<sup>633</sup> 48–52°.<sup>502.5</sup>  
 $p$ -O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCN, m. 54°.<sup>633</sup>  
 $m$ -MeC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCN, b<sub>0.6</sub> 138°; n 20/D 1.5471.<sup>633</sup>  
 $o$ -Me<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCN, b<sub>0.1</sub> 140°; n 20/D 1.5363.<sup>633</sup>  
 $c$ -HexC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCN, *o*-, b<sub>3</sub> 215–8°.<sup>1133</sup>  
 PhCH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCN, b<sub>0.1</sub> 124°; n 20/D 1.5348.<sup>633</sup>  
 $o$ -ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCN, b<sub>0.8</sub> 152°; n 20/D 1.5506.<sup>633</sup>  
 PhOCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>SCN, m. 39°; b<sub>0.1</sub> 155°; n 20/D 1.5480.<sup>633</sup>  
 ClC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>SCN, *o*-, b<sub>0.5</sub> 164°; n 20/D 1.5544; *m*-, b<sub>1.9</sub> 186°; n 20/D 1.5543.<sup>633</sup>  
 $p$ -BrC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>SCN, b<sub>0.5</sub> 180°; n 20/D 1.5410.<sup>487</sup>



$\text{MeC}_6\text{H}_4\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{SCN}$ , *o*-,  $b_{0.1}$  138°;  $n_{20/D}$  1.5533; *p*-,  $b_5$  193°;  $n_{20/D}$  1.5410.<sup>633</sup>

$\text{PhCH}_2\text{OCH}_2(\text{CH}_2)_3\text{CH}_2\text{SCN}$ ,  $b_{0.6}$  161°;  $n_{20/D}$  1.5292.<sup>633</sup>

### Silico Thiocyanates

$\text{Me}_3\text{SiCH}_2\text{SCN}$ ,  $b_1$  46°,  $b_{10}$  75°, <sup>1248.5</sup>  $b_{750}$  198.5°, <sup>1401</sup>  $b_{741}$  199°, <sup>1345</sup>  $b.$  196–7°; <sup>371</sup>  $d_{20/4}$  0.9466; <sup>371, 1401</sup>  $n_{20/D}$  1.4682, <sup>1401</sup> 1.4680, <sup>1248.5</sup> 1.4676.<sup>371</sup>

$\text{Et}_2\text{MeSiCH}_2\text{SCN}$ ,  $b_{1.5}$  72.5°, <sup>1401</sup>  $b_2$  72.5°; <sup>1401</sup>  $d_{20/4}$  0.9489;  $n_{20/D}$  1.4778.<sup>1401</sup>

$\text{Pr}_2\text{MeSiCH}_2\text{SCN}$ ,  $b_2$  84–6°;  $d_{20/4}$  0.9289;  $n_{20/D}$  1.4760.<sup>1248</sup>

$\text{Bu}_2\text{MeSiCH}_2\text{SCN}$ ,  $b_2$  106.5°;  $d_{20/4}$  0.9174;  $n_{20/D}$  1.4755.<sup>1248</sup>

$\text{Pr}_3\text{SiCH}_2\text{SCN}$ ,  $b_2$  120°;  $d_{20/4}$  0.9247;  $n_{20/D}$  1.4781.<sup>1248</sup>

$\text{Ph}_2\text{MeSiCH}_2\text{SCN}$ ,  $b_2$  172°;  $d_{20/4}$  1.1204;  $n_{20/D}$  1.5987.<sup>1248</sup>

$\text{Me}_3\text{SiOSiMe}_2\text{CH}_2\text{SCN}$ ,  $b_{42}$  135°;  $d_{20/4}$  0.9518;  $n_{20/D}$  1.4443.<sup>371</sup>

$\text{Me}_3\text{SiOSiMe}_2\text{OSiMe}_2\text{CH}_2\text{SCN}$ ,  $b_{47}$  168°;  $d_{20/4}$  1.045; <sup>1248</sup>  $n_{20/D}$  1.4370.<sup>371</sup>

$\text{Me}_2\text{OSiMe}_2\text{CH}_2\text{SCN}$ ,  $b_{1.5}$  105°;  $d_{20/4}$  1.0722;  $n_{20/D}$  1.4691.<sup>1248</sup>

$\text{Me}_3\text{SiCHMeSCN}$ ,  $b_5$  123°;  $d_{20/4}$  0.9380;  $n_{20/D}$  1.4702.<sup>1248</sup>

$\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SCN}$ ,  $b_1$  70°, <sup>1248.5</sup> 66.8°;  $d_{20/4}$  0.9278; <sup>1248</sup>  $n_{20/D}$  1.4685, <sup>1248</sup> 1.4690.<sup>1248.5</sup>

$\text{Et}_2\text{MeSiCH}_2\text{CH}_2\text{CH}_2\text{SCN}$ ,  $b_{1.5}$  85–6°;  $d_{20/4}$  0.9331;  $n_{20/D}$  1.4780.<sup>1248.5</sup>

$\text{Pr}_2\text{MeSiCH}_2\text{CH}_2\text{CH}_2\text{SCN}$ ,  $b_1$  116–8°;  $d_{20/4}$  0.9181;  $n_{20/D}$  1.4760.<sup>1248.5</sup>

$\text{Me}_3\text{SiCH}_2\text{CHMeCH}_2\text{SCN}$ ,  $b_{10}$  100–1°;  $d_{20/4}$  0.9239;  $n_{20/D}$  1.4710.<sup>1248.5</sup>

$\text{Et}_2\text{MeSiCH}_2\text{CHMeCH}_2\text{SCN}$ ,  $b_{1.5}$  82–7°;  $d_{20/4}$  0.9230;  $n_{20/D}$  1.4801.<sup>1248.5</sup>

### Sulfide Thiocyanates

$\text{PhSCH}_2\text{SCN}$ ,  $b_{0.5}$  118–20°.<sup>96</sup>

*p*- $\text{ClC}_6\text{H}_4\text{SCH}_2\text{SCN}$ , *m.* 75–7°.<sup>96, 1214</sup>

$\text{EtSCH}_2\text{CH}_2\text{SCN}$ ,  $b_5$  105–10°; <sup>1058</sup> sulfone, *m.* 39°.<sup>1058</sup>

$\text{PhSCH}_2\text{CH}_2\text{SCN}$ ,  $b_2$  143–6°; <sup>1058</sup> sulfone, *m.* 72°.<sup>1058</sup>

*p*- $\text{ClC}_6\text{H}_4\text{SCH}_2\text{CH}_2\text{SCN}$ , *m.* 36–8°.<sup>1821</sup>

$\text{Cl}_2\text{C}_6\text{H}_3\text{SCH}_2\text{CH}_2\text{SCN}$ , 2,5-,  $b_{12}$  215–20°; 3,4-,  $b_{12}$  213–16°.<sup>1821</sup>

2,4,5- $\text{Cl}_3\text{C}_6\text{H}_2\text{SCH}_2\text{CH}_2\text{SCN}$ , *m.* 26°;  $b_{12}$  225–30°.<sup>1725.5, 1821</sup>

*p*- $\text{ClC}_6\text{H}_4\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCN}$ ,  $b_1$  155–8°;  $n_{20/D}$  1.6065.<sup>1725.5, 1821</sup>

- $\text{Cl}_2\text{C}_6\text{H}_3\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCN}$ , 2,4-,  $b_{0.2}$  158–60°;  $n_{20/D}$  1.6200; 3,4-,  $b_{0.2}$  165–7°;  $n_{20/D}$  1.6240.<sup>1725.5, 1821</sup>  
 $\text{MeSCH}_2\text{CH}_2\text{CH}_2\text{SCN}$ , sulfone, m. 57°;  $b_4$  205°.<sup>250, 1592</sup>  
 $\text{EtSCH}_2\text{CH}_2\text{CH}_2\text{SCN}$ ,  $b_{10}$  115–20°; sulfone, m. 39.5–41°.<sup>1058</sup>  
 $\text{PrSCH}_2\text{CH}_2\text{CH}_2\text{SCN}$ ,  $b_{10}$  115–20°;  $d_{17/4}$  1.086;  $n_{17/D}$  1.5220.<sup>1058</sup>  
 $\text{PhSCH}_2\text{CH}_2\text{CH}_2\text{SCN}$ ,  $b_3$  176–8°;  $d_{16/4}$  1.160;  $n_{16/D}$  1.587; sulfone, m. 91°.<sup>1058</sup>  
 2-(*o*- $\text{O}_2\text{NC}_6\text{H}_4\text{S}$ )cyclohexylSCN, m. 84°.<sup>998</sup>  
 2-[2,4-( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3\text{S}$ ]cyclohexylSCN, m. 139.5°.<sup>998</sup>

### Aldehyde and Ketone Thiocyanates

- $\text{OCHCH}_2\text{SCN}$ ,  $d_{18}$  1.47.<sup>331</sup>  
 $\text{MeCOCH}_2\text{SCN}$ ,  $b_1$  73.5–74.5°; <sup>1759</sup> $d_0$  1.209, <sup>1760</sup>1.200, <sup>1757</sup> $d_{15/4}$  1.1881, <sup>1759</sup> $d_{20/4}$  1.180, <sup>1759</sup>1.182, <sup>1088</sup> $d_{20}$  1.195; <sup>1760</sup> $n_{20/D}$  1.4951; <sup>1721</sup>Oxime, *sym.*, m. 170°; *anti*, m. 135°.<sup>1423</sup>  
 $\text{MeCOCHPhSCN}$ , m. 52°.<sup>1838</sup>  
 $\text{MeCOCH}_2\text{CH}_2\text{SCN}$ ,  $b_8$  94–6°.<sup>1286.6</sup>  
 $\text{MeCOCH}_2\text{CMe}_2\text{SCN}$ ,  $b_9$  98–100°.<sup>260a</sup>  
 $\text{MeCOCH}_2\text{CHAmSCN}$ ,  $b_{1.5}$  109–12°.<sup>260a</sup>  
 $\text{MeCOCH}_2\text{CH}(\text{SCN})\text{CHEtBu}$ ,  $b_1$  122–3°.<sup>260a</sup>  
 $\text{MeCOC}(\text{SCN})\text{:CHPh}$ , m. 119°.<sup>318</sup>  
 $\text{MeCOCBr}(\text{SCN})\text{CHBrPh}$ , m. 138°.<sup>318</sup>  
 $\text{Me}_2\text{C:CHCOCH}_2\text{CMe}_2\text{SCN}$ ,  $b_1$  104–7°.<sup>260a</sup>  
 2-(2-Ethyl-1-thiocyanobutyl)cyclohexanone,  $b_{1.5}$  142°.<sup>260a</sup>  
 2-(1-Thiocyanocyclohexyl)cyclohexanone,  $b_{1.5-2}$  150–5°; <sup>260a</sup> $d_{25/4}$  1.0997;  $n_{20/D}$  1.5473.<sup>260a</sup>  
 $\text{ClCH}_2\text{COCH}_2\text{SCN}$ , m. 85°.<sup>1422</sup>  
 $2\text{-C}_4\text{H}_3\text{S}\cdot\text{COCH}_2\text{SCN}$ , m. 88°.<sup>258</sup>  
 Carvone-, m. 254°.<sup>318</sup>  
 4-Antipyril-, m. 146.5°.<sup>1740.5</sup>  
 21-Thiocyano-4-pregnene-3,20-diene, m. 175°.<sup>1461.5</sup>

### Amine Thiocyanates

- $\text{H}_2\text{NCH}_2\text{CH}_2\text{SCN}$ ,  $\text{HBr}$ , m. 172°; <sup>1603</sup> $\text{Bz}$ , m. 78–80°; <sup>1602</sup>Phthalimide, m. 113.5°; <sup>607</sup>108°.<sup>359</sup>  
 $\text{H}_2\text{NCH}_2\text{CH}_2\text{S}^+\text{CN}$ ,  $\text{Bz}$ , m. 80°.<sup>494</sup>  
 $\text{Et}_2\text{NCH}_2\text{CH}_2\text{SCN}$ ,  $b_2$  87°.<sup>524</sup>  
 $(\text{PhCH}_2)_2\text{NCH}_2\text{CH}_2\text{SCN}$ , m. 55°.<sup>1327.5</sup>  
 $\text{H}_2\text{NCH}_2\text{CHMeSCN}$ , Phthalimide, m. 89–93°.<sup>1629</sup>

$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{SCN}$ ,  $\text{HBr}$ , m.  $137^\circ$ ; picrate, m.  $128^\circ$ ; <sup>1602</sup>  
 Phthalimide, m.  $96-8^\circ$ .<sup>610</sup>  
 $\text{HN:CMech}_2\text{SCN}$ , m.  $42^\circ$ ;  $b_{3-4}$   $136^\circ$ , b.  $231-2^\circ$ ; Ac, m.  $134^\circ$ .<sup>1761</sup>  
 $\text{MeN:CMech}_2\text{SCN}$ ,  $\text{HI}$ , m.  $159.5^\circ$ .<sup>1761</sup>  
 $\text{H}_2\text{NCH}_2\text{CH}(\text{SCN})\text{CH}_2\text{NH}_2$ , m.  $248^\circ$  (dec).<sup>1188</sup>

### Miscellaneous Substituted Thiocyanates

$\text{Me}_3\text{SnCH}_2\text{SCN}$ ,  $b_4$   $104-5^\circ$ .<sup>1644</sup>  
 $\text{NCCH}_2\text{CH}_2\text{SCN}$ ,  $b_{18}$   $160^\circ$ ; n 25/D 1.5024.<sup>771.5</sup>  
 $\text{NCCH}_2\text{CH}_2\text{CH}_2\text{SCN}$ ,  $b_{30-40}$   $195^\circ$ ,  $b_{110-20}$   $220^\circ$ .<sup>606c</sup>

### PHENYL THIOCYANATES

Phenyl,  $\text{C}_6\text{H}_5\text{SCN}$ ,  $b_{1.5}$   $71-3^\circ$ ,<sup>1495.5</sup>  $b_2$   $61-6^\circ$ ,<sup>5</sup>  $b_8$   $89-90^\circ$ ,<sup>200</sup>  $b_9$   $94-7^\circ$ ,<sup>1495.5</sup>  $b_{14}$   $104-6^\circ$ ,<sup>1495.5</sup>  $b_{708}$   $231^\circ$ ,<sup>1813, 1814</sup> b.  $232-3^\circ$ ,<sup>1512</sup>  $232^\circ$ ,<sup>1512</sup>  $231^\circ$ ; <sup>1512</sup>  $d_{17.5}$  1.155,<sup>626</sup>  $d_{42.5/4}$  1.1228; <sup>1391</sup> n 25/D 1.5712; <sup>200</sup> dipole moment 3.59; <sup>144</sup> parachor 307.3; <sup>1391</sup> molecular heat of combustion at constant pressure 1037.4 cal.<sup>846</sup>  
 Chlorophenyl,  $\text{ClC}_6\text{H}_4\text{SCN}$ , *o*-,  $b_{42-7}$   $160^\circ$ ; *m*-,  $b_{12.5}$   $135^\circ$ ; <sup>320</sup> *p*-, m.  $36^\circ$ ; <sup>742</sup> dipole moment 2.93.<sup>144</sup>  
 2,4-Dichlorophenyl,  $\text{Cl}_2\text{C}_6\text{H}_3\text{SCN}$ , m.  $57^\circ$ .<sup>1746</sup>  
 Bromophenyl,  $\text{BrC}_6\text{H}_4\text{SCN}$ , *o*-, m.  $24^\circ$ ;  $b_{11}$   $161-5^\circ$ ; <sup>320</sup> *p*-, m.  $56^\circ$ .<sup>319</sup>  
*p*-Iodophenyl,  $\text{IC}_6\text{H}_4\text{SCN}$ , m.  $53^\circ$ ,<sup>320</sup>  $52^\circ$ ,<sup>319</sup>  $51^\circ$ .<sup>434a, b</sup>  
 Nitrophenyl,  $\text{O}_2\text{NC}_6\text{H}_4\text{SCN}$ , *o*-, m.  $132.7^\circ$ ,<sup>1486</sup>  $132.5^\circ$ ,<sup>1278</sup>  $136^\circ$ ,<sup>980</sup>  $130^\circ$ ; <sup>1951</sup> *m*-, m.  $56.1^\circ$ ,<sup>1486</sup>  $56^\circ$ ; <sup>220, 539</sup>  $b_{15}$   $180^\circ$ ,<sup>539</sup>  $b_{12}$   $170-3^\circ$ ; <sup>220</sup> *p*-, m.  $133^\circ$ .<sup>1278, 1487</sup>  
 2,4-Dinitrophenyl,  $(\text{O}_2\text{N})_2\text{C}_6\text{H}_3\text{SCN}$ , m.  $140^\circ$ ,<sup>1487</sup>  $139^\circ$ ,<sup>68, 319, 812, 1828.5</sup>  $80.5-2.5^\circ$ .<sup>997.5, 1507</sup>  
 2,4,6-Trinitrophenyl,  $(\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{SCN}$ , needles, darken at about  $285^\circ$ .<sup>386</sup>  
 Nitrochlorophenyl,  $\text{O}_2\text{N}(\text{Cl})\text{C}_6\text{H}_3\text{SCN}$ , 2,4-, m.  $117^\circ$ ,<sup>1949</sup>  $116.5^\circ$ ; <sup>319</sup> 3,4-, m.  $63^\circ$ .<sup>321, 579</sup>  
 Nitrobromophenyl,  $\text{O}_2\text{N}(\text{Br})\text{C}_6\text{H}_3\text{SCN}$ , 2,4-, m.  $131^\circ$ ; <sup>319</sup> 3,4-, m.  $83^\circ$ .<sup>321</sup>  
*p*-Hydroxyphenyl,  $\text{HOC}_6\text{H}_4\text{SCN}$ , m.  $63^\circ$ ,<sup>200</sup>  $62^\circ$ ,<sup>200</sup>  $60^\circ$ ,<sup>1929</sup>  $58^\circ$ ,<sup>857</sup>  $54^\circ$ ,<sup>1685</sup>  $53^\circ$ .<sup>37</sup>  $\frac{1}{2}\text{H}_2\text{O}$ , m.  $54^\circ$ .<sup>1683.5</sup>  
 3,4- $(\text{HO}_2\text{C}_6\text{H}_3\text{SCN})$ , m.  $142^\circ$ ; <sup>1179, 1316</sup> diAc, m.  $58^\circ$ .<sup>1179</sup>  
 3,4,5- $\text{O}_2\text{N}(\text{HO})\text{ClC}_6\text{H}_2\text{SCN}$ , m.  $87.8^\circ$ .<sup>1507</sup>  
 3,4,5- $\text{O}_2\text{N}(\text{HO})\text{BrC}_6\text{H}_2\text{SCN}$ , m.  $91-5^\circ$ .<sup>1507</sup>  
*p*- $\text{MeOC}_6\text{H}_4\text{SCN}$ , m.  $35^\circ$ ,<sup>1229</sup>  $33^\circ$ .<sup>434c</sup>

- $p$ -PhOC<sub>6</sub>H<sub>4</sub>SCN, m. 48°. <sup>790</sup>  
 MeO(HO)C<sub>6</sub>H<sub>3</sub>SCN, 3,4-, m. 107°. <sup>538</sup>  
 $p$ -NCSC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NHC(:NH)NH<sub>2</sub>, m. 170–2°. <sup>483.5</sup>  
 $o$ -NCC<sub>6</sub>H<sub>4</sub>SCN, m. 83°. <sup>45</sup>

## ACYL THIOCYANATES

- Propionyl, EtCOSCNCN, b. 149–50°; n 20/D 1.5152. <sup>1132.5</sup>  
*i*-Butyryl, Me<sub>2</sub>CHCOSCNCN, b. 159–61°; n 20/D 1.5075. <sup>1132.5</sup>  
*i*-Valeryl, *i*-BuCOSCNCN, b. 60–1°; n 18/D 1.5032. <sup>1132.5</sup>  
 Pivalyl, Me<sub>3</sub>CCOOH, b. 163–6°; n 20/D 1.5020. <sup>1132.5</sup>  
 AmCOSCNCN, b. 89–90°; n 20/D 1.5003. <sup>1132.5</sup>  
 PrMeCHCOSCNCN, b. 78–9°; n 27/D 1.4940. <sup>1132.5</sup>  
 EtMe<sub>2</sub>CCOSCNCN, b. 69–70°; n 20/D 1.5010. <sup>1132.5</sup>  
 HexCOSCNCN, b. 119–20°; n 20/D 1.5003. <sup>1132.5</sup>  
 PrMe<sub>2</sub>CCOSCNCN, b. 84–5°; n 20/D 1.4960. <sup>1132.5</sup>  
 HeptCOSCNCN, b. 122–3°; n 20/D 1.4930. <sup>1132.5</sup>  
 EtBuCHCOSCNCN, b. 101–2°; n 20/D 1.4940. <sup>1132.5</sup>  
 OctCOSCNCN, b. 133–5°; n 23/D 1.4985. <sup>1132.5</sup>  
 NonCOSCNCN, b. 130–1°; n 23/D 1.4845. <sup>1132.5</sup>  
 DecCOSCNCN, b. 143–4°; n 22/D 1.4899. <sup>1132.5</sup>  
 C<sub>11</sub>H<sub>23</sub>COSCNCN, b. 153–4°; n 20/D 1.4892. <sup>1132.5</sup>  
 C<sub>13</sub>H<sub>27</sub>COSCNCN, b. 175–7°; n 20/D 1.4898. <sup>1132.5</sup>  
 C<sub>15</sub>H<sub>33</sub>COSCNCN, b. 183–5°. <sup>1132.5</sup>  
 PhCH<sub>2</sub>COSCNCN, b. 129–30°; n 20/D 1.5943. <sup>1132.5</sup>  
 PhCH<sub>2</sub>CH<sub>2</sub>COSCNCN, b. 148–50°; n 20/D 1.5840. <sup>1132.5</sup>  
 PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COSCNCN, b. 130–1°; n 20/D 1.5748. <sup>1132.5</sup>  
 TricyclenylCOSCNCN, b. 113–4°; n 20/D 1.5616. <sup>1132.5</sup>  
 EtCH:CHCOSCNCN, b. 86–8°; n 28/D 1.5440. <sup>1132.5</sup>  
 PrCH:CHCOSCNCN, b. 99–100°; n 22/D 1.5410. <sup>1132.5</sup>  
 BuCH:CHCOSCNCN, b. 110–11°; n 20/D 1.5308. <sup>1132.5</sup>  
 AmCH:CHCOSCNCN, b. 112°; n 20/D 1.5249. <sup>1132.5</sup>  
 PrCH(Me)CH:CHCOSCNCN, b. 123–4°; n 22/D 1.5285. <sup>1132.5</sup>  
 HexCH:CHCOSCNCN, b. 108–9°; n 20/D 1.5258. <sup>1132.5</sup>  
 HeptCH:CHCOSCNCN, b. 128–9°; n 21/D 1.5250. <sup>1132.5</sup>  
 OctCH:CHCOSCNCN, b. 130–2°; n 24/D 1.5190. <sup>1132.5</sup>  
 DecCH:CHCOSCNCN, b. 159–61°; n 28/D 1.5033. <sup>1132.5</sup>  
 PrCH:CEtCOSCNCN, b. 116–7°; n 24/D 1.5324. <sup>1132.5</sup>  
 SorbylCOSCNCN, b. 70°. <sup>1132.5</sup>  
 FurylCOSCNCN, b. 109–10°; n 21/D 1.6326. <sup>1132.5</sup>  
 3-PyridylCOSCNCN, b. 106°; n 20/D 1.6421. <sup>1132.5</sup>

3-FurylCH:CHCOSC*N*, *b*<sub>1</sub> 116–7°.<sup>1132.5</sup>  
 3-ThienylCH:CHCOSC*N*, *b*<sub>3</sub> 150–1°.<sup>1132.5</sup>  
 CF<sub>3</sub>COSC*N*, *b*. 72–4°; *d*<sub>25</sub> 1.369.<sup>1381</sup>  
 CF<sub>3</sub>CF<sub>2</sub>COSC*N*, *b*. 87°; *d*<sub>25</sub> 1.503.<sup>1381</sup>  
 CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>COSC*N*, *b*. 106°; *d*<sub>25</sub> 1.644.<sup>1381</sup>  
*p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>COSC*N*, *m*. 90–2°; *b*<sub>10</sub> 187–8°.<sup>1287</sup>  
*p*-MeOC<sub>6</sub>H<sub>4</sub>COSC*N*, *b*<sub>10</sub> 169–70°; *n* 24/D 1.6510.<sup>1132.5</sup>  
 (MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>COSC*N*, *m*. 64.2°; *b*<sub>6</sub> 150–3°.<sup>1132.5</sup>

## ANILINE THIOCYANATES

*p*-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SC*N*, *m*. 97°;<sup>958, 959, 960</sup> 58°;<sup>868, 974, 983</sup> 57.5°;<sup>1685</sup>  
 57°; 289, 731, 1129, 1316, 1486 Ac, *m*. 187°;<sup>1286.5</sup> Nitrobenzamide, *o*-,  
*m*. 240°; *m*-, *m*. 199°; *p*-, *m*. 238°;<sup>947</sup> N-chaulmoogryl, *m*.  
 52°;<sup>49b</sup> *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NHCO—, *m*. 136–8°.<sup>946.7</sup>  
*p*-(MeSO<sub>2</sub>NHC<sub>6</sub>H<sub>4</sub>SC*N*, *m*. 102°.<sup>1230.5</sup>  
*p*-(*p*-ClC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)NHC<sub>6</sub>H<sub>4</sub>SC*N*, *m*. 130°.<sup>1230.5</sup>  
*p*-(*p*-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NH)C<sub>6</sub>H<sub>4</sub>SC*N*, *m*. 192°;<sup>1744a</sup> Ac, *m*. 208°.<sup>1744a</sup>  
 PhN=NC<sub>6</sub>H<sub>4</sub>SC*N*, *o*-, *m*. 99–101°.<sup>310</sup>  
*o*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>N=NC<sub>6</sub>H<sub>4</sub>SC*N*, *m*. 144°.<sup>271</sup>  
*p*-HO(N:)NC<sub>6</sub>H<sub>4</sub>SC*N*, explodes at 110–14°.<sup>742</sup>  
*p*-H<sub>2</sub>NNHC<sub>6</sub>H<sub>4</sub>SC*N*, *m*. 96°.<sup>835a</sup>  
*p*-EtNHC<sub>6</sub>H<sub>4</sub>SC*N*, *m*. 58°.<sup>1230</sup>  
*p*-C<sub>16</sub>H<sub>33</sub>NHC<sub>6</sub>H<sub>4</sub>SC*N*, *m*. 67°.<sup>49a, b</sup>  
*p*-C<sub>18</sub>H<sub>35</sub>NHC<sub>6</sub>H<sub>4</sub>SC*N*, *m*. 62°.<sup>49a, b</sup>  
*p*-PhCH<sub>2</sub>NHC<sub>6</sub>H<sub>4</sub>SC*N*, *m*. 78°.<sup>977</sup>  
*p*-HOCH<sub>2</sub>CH<sub>2</sub>NHC<sub>6</sub>H<sub>4</sub>SC*N*, *m*. 63°.<sup>137.5</sup>  
*p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SC*N*, *m*. 75°;<sup>289</sup> 64.5°;<sup>239, 1092, 1129, 1316, 1685, 1929</sup>  
 74°;<sup>1316</sup> 73°;<sup>538, 1400</sup> 72–73°.<sup>37</sup>  
*p*-Et<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SC*N*, *b*<sub>1</sub> 138°.<sup>538</sup>  
*p*-PhCH<sub>2</sub>(Me)NC<sub>6</sub>H<sub>3</sub>SC*N*, *m*. 69°;<sup>1254.5</sup> 63°.<sup>977</sup>  
*p*-PhCH<sub>2</sub>(Et)NC<sub>6</sub>H<sub>3</sub>SC*N*, *m*. 54°;<sup>977</sup> 53°.<sup>1254.5</sup>  
 4,3-H<sub>2</sub>N(HO)C<sub>6</sub>H<sub>3</sub>SC*N*, H<sub>2</sub>NCO—, *m*. 162°; H<sub>2</sub>NCS—, *m*. 138°;  
 PhNHCO—, *m*. 182°.<sup>949</sup> (HO(NCS)C<sub>6</sub>H<sub>3</sub>NH)<sub>2</sub>CO, *m*. 174°.<sup>949</sup>  
 2,5-H<sub>2</sub>N(HO)C<sub>6</sub>H<sub>3</sub>SC*N*, *m*. 121°; 2-Ac, *m*. 206° dec.; diAc, *m*.  
 183°.<sup>537</sup>  
 2,5-(β,α-HOC<sub>10</sub>H<sub>6</sub>N:N)(HO)C<sub>6</sub>H<sub>3</sub>SC*N*, *m*. 130°.<sup>537</sup>  
 2,5-H<sub>2</sub>N(EtO)C<sub>6</sub>H<sub>3</sub>SC*N*, *m*. 68°.<sup>983</sup>  
 4,2-H<sub>2</sub>N(Cl)C<sub>6</sub>H<sub>3</sub>SC*N*, *m*. 75°;<sup>1741.5</sup> 61°.<sup>1497</sup>  
 4,3,5-H<sub>2</sub>N(Br<sub>2</sub>)C<sub>6</sub>H<sub>2</sub>SC*N*, *m*. 118°.<sup>434</sup>  
 4,3-H<sub>2</sub>N(O<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>SC*N*, *m*. 113°;<sup>529</sup> Ac, *m*. 139°;<sup>579</sup> Bz, *m*.

139°; Nitrobenzamide, *m*-, m. 148°; *p*-, m. 175°;<sup>946.7</sup>  
 PhNHCO—, m. 118°; *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NHCO—, m. 115°.<sup>946.7</sup>  
 4-Thiocyano-*m*-phenylenediamine, (H<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SCN, m. 161°.<sup>1129</sup>  
 2,4,5-(H<sub>2</sub>N)<sub>2</sub>(HO)C<sub>6</sub>H<sub>2</sub>SCN, 2,4-DiAc, m. 217°; triAc, m.  
 156°.<sup>537</sup>

#### BENZYL THIOCYANATES

PhCH<sub>2</sub>SCN, m. 43.5°;<sup>1878</sup> 41°;<sup>94</sup> 36–8°;<sup>779a</sup> b. 256°;<sup>558</sup> 230–35°  
 (dec),<sup>558</sup> 235°.<sup>94</sup>  
 ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SCN, *o*-, b<sub>5</sub> 138–41°; n 25/D 1.5878;<sup>1746</sup> *m*-, b<sub>2</sub> 142–  
 5°; n 25/D 1.5827°;<sup>1746</sup> *p*-, m. 17°.<sup>888</sup>  
 BrC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SCN, *o*-, oil;<sup>890</sup> *p*-, m. 25°.<sup>889</sup>  
*p*-IC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SCN, m. 40°.<sup>1162</sup>  
 NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SCN, *o*-, m. 138°.<sup>307</sup>  
 O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SCN, *o*-, m. 75°;<sup>307</sup> 71°;<sup>558</sup> *m*-, m. 76°;<sup>1158</sup> *p*-, m.  
 86°;<sup>891</sup> 85.5°;<sup>1161</sup> 84°;<sup>138</sup> 79°.<sup>558</sup>  
 2,4(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>SCN, m. 87°.<sup>891</sup>  
*p*-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SCN, b<sub>0.5</sub> 109°.<sup>1327</sup>  
 (HO)Br<sub>2</sub>C<sub>6</sub>H<sub>2</sub>SCN, 2,3,5-, m. 112°; 4,3,5-, m. 109°.<sup>1709</sup>  
 3,2,4,6-(HO)Br<sub>3</sub>C<sub>6</sub>HCH<sub>2</sub>SCN, m. 122°.<sup>1709</sup>  
*p*-MeSC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SCN, m. 55°.<sup>889</sup>  
 PhCH(CN)SCN, m. 65°.<sup>360</sup>  
*o*-NCC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SCN, m. 86°.<sup>409</sup>  
 MeC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SCN, *o*-, m. 18.5°;<sup>1726b</sup> b<sub>12</sub> 147°;<sup>1877b</sup> b<sub>30</sub> 170°;<sup>1762b</sup>  
*p*-, m. 22.5°.<sup>1726b</sup>  
 Mesityl, 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>SCN, m. 58°.<sup>1877a, b, c</sup>  
 5,2,3-Me(HO)(ClCH<sub>2</sub>)C<sub>6</sub>H<sub>2</sub>CH<sub>2</sub>SCN, m. 103°.<sup>1945</sup>  
 3,6,5-Me(HO)(HOCH<sub>2</sub>)C<sub>6</sub>H<sub>2</sub>CH<sub>2</sub>SCN, m. 86°.<sup>1945</sup>  
 Ph<sub>2</sub>CHSCN, m. 59°; b<sub>2</sub> 160–70°.<sup>782</sup>

#### TOLYL AND XYLIL THIOCYANATES

Tolyl, MeC<sub>6</sub>H<sub>4</sub>SCN, *o*-, b<sub>765</sub> 243–6°;<sup>1778</sup> *p*-, b<sub>40–50</sub> 155–58,<sup>1459</sup> b.  
 240–5°.<sup>1459</sup>  
 Me(HO)C<sub>6</sub>H<sub>3</sub>SCN, 3,4-, m. 71°;<sup>961</sup> 3,5-, m. 76°.<sup>961</sup>  
 3,4-Me(MeO)C<sub>6</sub>H<sub>3</sub>SCN, b<sub>8</sub> 150–60°; d 20/4 1.209;<sup>1229</sup> n 20/D  
 1.5870.<sup>1229</sup>  
 Me(O<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>SCN, 2,4-, m. 118.5°;<sup>821</sup> 2,5-, m. 70.5°;<sup>821</sup> 2,6-,  
 m. 47°;<sup>1118</sup> 45.5°;<sup>194</sup> 3,2-, m. 86°;<sup>194</sup> 4,2-, m. 125°.<sup>194, 319</sup>  
 Me(H<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>SCN, 2,4-, m. 83°;<sup>1400</sup> 3,4-, m. 70°.<sup>1400</sup>

2,4-Me (*p*-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NH)C<sub>6</sub>H<sub>3</sub>SCN, m. 155°; Ac, m. 229°. <sup>1744a</sup>  
 2,6,4-Me<sub>2</sub>(HO)C<sub>6</sub>H<sub>2</sub>SCN, m. 128.5°. <sup>1022</sup>  
 2,6,3,4-Me<sub>2</sub>(O<sub>2</sub>N)(HO)C<sub>6</sub>HSCN, m. 187.5°. <sup>1507</sup>  
 2,6,3,4,5-Me<sub>2</sub>(O<sub>2</sub>N)(HO)BrC<sub>6</sub>SCN, m. 156.5°. <sup>1507</sup>  
 Me<sub>2</sub>(H<sub>2</sub>N)C<sub>6</sub>H<sub>2</sub>SCN, 3,5,4-, m. 88°. <sup>1022</sup>

## OTHER ARYL THIOCYANATES

α-Methylbenzyl, PhCHMeSCN, b<sub>36</sub> 157-9°. <sup>1877</sup>  
 Phenethyl, PhCH<sub>2</sub>CH<sub>2</sub>SCN, b<sub>3</sub> 116-8°, <sup>1764</sup> b<sub>20</sub> 161-3°; <sup>1746</sup> d 20/4 1.2158; <sup>1764</sup> n 25/D 1.5598. <sup>1746</sup>  
 PhC(SCN):CHNO<sub>2</sub>, m. 89°. <sup>1390.5</sup>  
 3-Phenylpropyl, PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCN, b<sub>30</sub> 80°. <sup>127a, b</sup>  
 ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCN, *o*-, b<sub>0.5</sub> 164°; n 20/D 1.5544°; <sup>633</sup>  
*m*-, b<sub>1.9</sub> 186°; n 20/D 1.5543. <sup>633</sup>  
*p*-BrC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCN, b<sub>0.5</sub> 180°; n 20/D 1.5410. <sup>633</sup>  
 MeC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCN, *o*-, b<sub>0.1</sub> 138°; n 20/D 1.5533; *p*-,  
 b<sub>5.0</sub> 193°; n 20/D 1.5410. <sup>633</sup>  
*p*-Me<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>SCN, b<sub>18</sub> 170-2°; n 25/D 1.5509. <sup>1746</sup>  
 2,3,4-(EtMeCH)(O<sub>2</sub>N)(HO)C<sub>6</sub>H<sub>2</sub>SCN, m. 81.4°. <sup>1507</sup>  
 2,5,4-Me(Me<sub>2</sub>CH)(HO)C<sub>6</sub>H<sub>2</sub>SCN, m. 109°. <sup>965</sup>  
 2,5,4-Me(Me<sub>2</sub>CH)(MeO)C<sub>6</sub>H<sub>2</sub>SCN, b<sub>10</sub> 180-90°; d 20/4 1.149  
 n 20/D 1.5660. <sup>1229</sup>  
*sym*-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>SCN, m. 72°. <sup>1683.5</sup>  
 Ph<sub>3</sub>CSCN, m. 137.5°, <sup>157</sup> 137°; <sup>235, 492</sup> b<sub>4</sub> 203°. <sup>157</sup>  
 (*p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)Ph<sub>2</sub>CSCN, m. 115°. <sup>85</sup>  
 (*p*-MeOC<sub>6</sub>H<sub>4</sub>)Ph<sub>2</sub>CSCN, m. 72°. <sup>1126</sup>  
 (*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>CSCN, m. 148°. <sup>1270</sup>  
 Naphthyl, C<sub>10</sub>H<sub>7</sub>SCN, m. 55°, <sup>324</sup> 54°; <sup>324</sup> m. 75°, <sup>158a</sup> 35.9°. <sup>1477a</sup>  
 1,4-ClC<sub>10</sub>H<sub>6</sub>SCN, oil. <sup>1950</sup>  
 HOC<sub>10</sub>H<sub>6</sub>SCN, 2,1-, m. 68-70°, <sup>472a</sup> 1,4-, m. 118°, <sup>865c</sup> 114°. <sup>970a</sup>  
 2,1-MeOC<sub>10</sub>H<sub>6</sub>SCN, m. 134°. <sup>972a</sup>  
 2,6,1-MeO(Cl)C<sub>10</sub>H<sub>5</sub>SCN, m. 43°. <sup>811</sup>  
 1,4-H<sub>2</sub>NC<sub>10</sub>H<sub>6</sub>SCN, m. 142°; <sup>1400</sup> H<sub>2</sub>NCO—, m. 259°;  
 PhNHCO—, m. 250°; <sup>949</sup> H<sub>2</sub>NCS—, m. 250°; OC(NHC<sub>10</sub>-  
 H<sub>6</sub>SCN)<sub>2</sub>, m. 252°. <sup>949</sup>  
 C<sub>10</sub>H<sub>7</sub>CH<sub>2</sub>SCN, α m. 91.5°. <sup>1683.5</sup>  
 PhC<sub>6</sub>H<sub>4</sub>SCN, *o*-, b. 109-11°; <sup>209</sup> *p*-, m. 84°. <sup>608</sup>  
 Tetralyl-6-methyl-thiocyanate, MeC<sub>10</sub>H<sub>11</sub>SCN, b. 168-74°. <sup>926</sup>  
 9-Thiocyanoanthracene, C<sub>14</sub>H<sub>9</sub>SCN, m. 181°. <sup>558</sup>  
 3-Pyrenylthiocyanate, C<sub>16</sub>H<sub>9</sub>SCN, m. 118°. <sup>1154</sup>

## HETEROCYCLIC THIOCYANATES

## 3-Chloromethyl-3-thiocyanomethyloxetane

$\overline{\text{OCH}_2\text{C}(\text{CH}_2\text{Cl})(\text{CH}_2\text{SCN})\text{CH}_2}$ ,  $b_{1.5}$  115°;  $n_{25/D}$  1.5298.<sup>291.5</sup>

Thiocyanotetrahydrofuran,  $\text{C}_4\text{H}_7\text{O}\cdot\text{SCN}$ ,  $b_{18}$  122–2.5°.<sup>1640, 1641</sup>

2- $\text{C}_4\text{H}_7\text{O}\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{SCN}$ ,  $b_4$  118–9°.<sup>1640, 1641</sup>

2- $\text{C}_4\text{H}_3\text{O}\cdot\text{CH}(\text{SCN})\text{CH}_2\text{NCS}$ ,  $m$ . 77°.<sup>1640</sup>

*p*-Thiocyano-5-nitro-2-furanilide,  $m$ . 156°.<sup>525.5</sup>

(Thiocyanomethyl)-tetrahydropyran,  $\text{C}_5\text{H}_9\text{O}\cdot\text{CH}_2\text{SCN}$ , 2-,  $b_4$  104°;  $d_{21/4}$  1.1303;  $n_{21/D}$  1.550; 3-,  $b_2$  109°;  $d_{21.5/4}$  1.144;  $n_{22/D}$  1.5097.<sup>1075.5</sup>

3-Nitro-2-thiocyano-5-chlorothiophene,  $(\text{O}_2\text{N})\text{ClC}_4\text{HS}\cdot\text{SCN}$ ,  $m$ . 86.6°.<sup>1214</sup>

2,5- $\text{H}_2\text{NC}_4\text{H}_2\text{S}\cdot\text{SCN}$ ,  $\text{Ac}$ ,  $m$ . 201–3° dec.<sup>852</sup>

2- $\text{C}_4\text{H}_3\text{S}\cdot\text{CH}_2\text{SCN}$ ,  $b_7$  100–2°,<sup>1497</sup>  $b_8$  104°,<sup>336</sup>  $b_{12}$  108–10°,<sup>1683.5</sup>  $b$ . 220–30°; <sup>336</sup>  $n_{21/D}$  1.595.<sup>336</sup>

5,2- $\text{ClC}_4\text{H}_2\text{S}\cdot\text{CH}_2\text{SCN}$ ,  $b_{1.4}$  123°;  $d_{25/4}$  1.379;  $n_{25/D}$  1.6242.<sup>287</sup>

3-Thiocyanomethyl-benzothiophene,  $b_{2-2.5}$  172–6°;  $n_{25/D}$  1.6790.<sup>1574</sup>

6-Methyl-8-thiocyanomethyl-2-phenyl-1,3-benzodioxane,  $m$ . 111.5°.<sup>1945</sup>

$\overline{\text{ClC}_6\text{H}_3\text{CH}_2\text{SCH}_2\text{CH}(\text{SCN})\text{CH}_2\text{O}}$ ,  $m$ . 50°.<sup>1065</sup>

3-Thiocyanopyrrole,  $m$ . 41.5–3°,<sup>1208</sup> 40–4°.<sup>1208</sup>

5-Thiocyanoindoline,  $m$ . 65°.<sup>1764.7</sup>

3-Thiocyanocarbazole,  $m$ . 112.7°.<sup>1251</sup>

Nitro-2-pyridylthiocyanate, 3-,  $m$ . 120°; 5-,  $m$ . 130°.<sup>1740</sup>

3,5-Dinitro-2-pyridylthiocyanate,  $m$ . 146°.<sup>1743</sup>

3-Thiocyanopyridine,  $m$ . 32°;  $b_{12}$  124°.<sup>1368</sup>

2-Thiocyanopyridine-1-oxide,  $m$ . 158–60°.<sup>1108</sup>

4-Nitro-2-thiocyanopyridine-1-oxide,  $m$ . 181°.<sup>1108</sup>

4-Thiocyanopyridine-1-oxide,  $m$ . 130–2°.<sup>1108</sup>

5-Thiocyano-8-quinolinol,  $m$ . 147°.<sup>1832</sup>

4-Thiocyanoquinoline-1-oxide,  $m$ . 155–7°.<sup>1331</sup>

Cincophenthioyanate, dec. at 186°.<sup>340</sup>

Methyl-5-thiocyano-8-quinolinol, 2-,  $m$ . 158°; 3-,  $m$ . 166°; 4-,  $m$ . 203°.<sup>534</sup>

2-Phenyl-5-thiocyano-8-quinolinol,  $m$ . 162°.<sup>534</sup>

2-Styryl-5-thiocyano-8-quinolinol,  $m$ . 196°.<sup>534</sup>



- 2-Methyl-5,7-dibromo-5-thiocyano-8-quinolinol, m.  $159^{\circ}$ .<sup>534</sup>  
 4-Amino-6-chloroquinaldinethiocyanate, m.  $212-14^{\circ}$ .<sup>620.5</sup>  
 2,3-Dimethyl-5-thiocyano-8-quinolinol, m.  $219^{\circ}$ .<sup>534</sup>  
 1-Thiocyanophthalazine, m.  $130^{\circ}$ ; b<sub>0.008</sub>  $180-205^{\circ}$ .<sup>1026</sup>  
 2-Chloro-4-thiocyano-5-nitropyrimidine, m.  $141^{\circ}$ .<sup>1741.6</sup>  
 6-Thiocyano-4-methyl-2-*p*-tolyl-pyrimidine, m.  $123^{\circ}$ .<sup>924</sup>  
 6-Purinythiocyanate, dec. about  $235^{\circ}$ .<sup>495.5</sup>

## 5-THIOCYANO-THIAZOLES

- 2-Amino-, m.  $145^{\circ}$ .<sup>1744b</sup> dec.  $150^{\circ}$ ; <sup>1745</sup> 2-Ac, m.  $210-5^{\circ}$ ; <sup>1744b</sup> 2-Bz, m.  $177^{\circ}$ .<sup>1744b</sup>  
 2-Benzamido-4-methyl-, m.  $199^{\circ}$ .<sup>1744b</sup>  
 2-Amino-4-phenyl-, m.  $186-8^{\circ}$ .<sup>1181.5</sup>  
 2-Amino-4-(*p*-tolyl)-, m.  $178^{\circ}$ .<sup>1181.5</sup>  
 2-Amino-4-(*p*-EtC<sub>6</sub>H<sub>4</sub>)-, m.  $156-8^{\circ}$ .<sup>1181.5</sup>  
 2-Amino-4-(3,4-xylyl)-, m.  $235^{\circ}$ .<sup>1181.5</sup>  
 2-Amino-4-(*o*-HOC<sub>6</sub>H<sub>4</sub>)-, m.  $260^{\circ}$ .<sup>1181.5</sup>  
 2-Amino-4-(*p*-MeOC<sub>6</sub>H<sub>4</sub>)-, m.  $243-5^{\circ}$ .<sup>1181.5</sup>  
 2-Amino-4-(*p*-EtOC<sub>6</sub>H<sub>4</sub>)-, m.  $244-6^{\circ}$ .<sup>1181.5</sup>  
 2-Acetamido-4-(*p*-ClC<sub>6</sub>H<sub>4</sub>)-, m.  $225^{\circ}$  (dec).<sup>405, 1181.5</sup>  
 2-Amino-4-(*p*-BrC<sub>6</sub>H<sub>4</sub>)-, m.  $276^{\circ}$ .<sup>1181.5</sup>  
 2-Amino-4-(H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)-, *m*-, m.  $278^{\circ}$ ; *p*-, softens at  $300^{\circ}$ .<sup>1181.5</sup>  
 2-Amino-4-(Naphthyl)-,  $\alpha$ -, m.  $208^{\circ}$ ;  $\beta$ -, m.  $200^{\circ}$ ; <sup>1181.5</sup> Ac, m.  $300^{\circ}$ .<sup>1528</sup>  
 2-Amino-4-Phenethyl-, m.  $174^{\circ}$ .<sup>1181.5</sup>  
 2-Amino-4-(*p*-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>)-, m.  $192^{\circ}$ .<sup>1181.5</sup>  
 2-Amino-4-(2-Thienyl)-, m.  $202^{\circ}$ .<sup>1181.5</sup>

## BENZOTHAZOLES

- 6-Thiocyano-, m.  $188^{\circ}$ .<sup>1722</sup>  
 2-Amino-6-thiocyano-, m.  $188^{\circ}$ ; 2-Ac, m.  $247-9^{\circ}$ .<sup>1722, 1722.5</sup>

## AROMATIC THIOCYANO-ALDEHYDES AND -KETONES

- Thiocyanobenzaldehyde, HCOC<sub>6</sub>H<sub>4</sub>SCN, *o*-, m.  $76^{\circ}$ ; *p*-, m.  $78^{\circ}$ .<sup>581</sup>  
 3,4-O<sub>2</sub>N(HCO)C<sub>6</sub>H<sub>3</sub>SCN, m.  $108^{\circ}$ .<sup>1491.6</sup>  
 MeCOC<sub>6</sub>H<sub>4</sub>SCN, *o*-, m.  $61^{\circ}$ ; <sup>45</sup> *p*-, m.  $82^{\circ}$ .<sup>1607</sup>  
 H<sub>2</sub>N(MeCO)C<sub>6</sub>H<sub>3</sub>SCN, 4,2-, m.  $140^{\circ}$ ; Ac, m.  $213^{\circ}$ ; 4,3-, m.  $106^{\circ}$ ; 2,5-, m.  $133-40^{\circ}$ .<sup>1491</sup>  
 PhCOCH<sub>2</sub>SCN, m.  $76^{\circ}$ ,<sup>1737.5</sup>  $75^{\circ}$ ,<sup>1854</sup>  $74.6^{\circ}$ ,<sup>1460</sup>  $74^{\circ}$ ,<sup>466</sup>  $73^{\circ}$ .<sup>406</sup>

- $p$ -ClC<sub>6</sub>H<sub>4</sub>COCH<sub>2</sub>SCN, m. 139°;<sup>935</sup> 135°.<sup>1460</sup>  
 $p$ -BrC<sub>6</sub>H<sub>4</sub>COCH<sub>2</sub>SCN, m. 149°;<sup>1460</sup> 146.5°.<sup>935</sup>  
 $p$ -IC<sub>6</sub>H<sub>4</sub>COCH<sub>2</sub>SCN, m. 155°.<sup>1460</sup>  
 $m$ -O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>COCH<sub>2</sub>SCN, m. 124°;<sup>1460</sup> 119°.<sup>257</sup>  
 3,4-(HO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COCH<sub>2</sub>SCN, m. 147–50°.<sup>477</sup>  
 2,3,4-(HO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>COCH<sub>2</sub>SCN, m. 196°.<sup>477</sup>  
 $p$ -MeOC<sub>6</sub>H<sub>4</sub>COCH<sub>2</sub>SCN, m. 121°.<sup>257</sup>  
 PhCOCHPhSCN, m. 111°.<sup>1877b</sup>  
 $p$ -MeC<sub>6</sub>H<sub>4</sub>COCH<sub>2</sub>SCN, m. 106.8°.<sup>1460</sup>  
 2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COCH<sub>2</sub>SCN, m. 81°.<sup>1460</sup>  
 $\beta$ -C<sub>10</sub>H<sub>7</sub>COCH<sub>2</sub>SCN, m. 110°.<sup>1460</sup>  
 PhCOCH<sub>2</sub>CH(SCN)Ph, m. 89°.<sup>1535</sup>  
 3,4-Me(O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CO)C<sub>6</sub>H<sub>3</sub>SCN,  $o$ -, m. 149°;  $m$ -, m. 157°;  $p$ -, m. 209°.<sup>947</sup>  
 $\alpha$ -Thiocyanoindanone, m. 92°.<sup>1710</sup>  
 $\alpha$  Thiocyanotetralone, m. 56–68°.<sup>1710</sup>

#### ANTHRAQUINONE THIOCYANATES

- Thiocyananthraquinone, 1-, m. 241°;<sup>624b</sup> 231°;<sup>117a</sup> 2-, m. 206°;<sup>117a</sup> 205°.<sup>624b</sup>  
 1-Thiocyano-5-chloro-, m. 287°.<sup>624b</sup>  
 1-Thiocyano-amino-, 4-, m. 256°; Ac, m. 263°; 5-, m. 235°.<sup>624b</sup>  
 1-Thiocyano-methylamino-, 4-, m. 243°; 5-, m. 268°.<sup>624b</sup>  
 1-Thiocyano-dimethylamino-, 4-, m. 241°; 5-, m. 212°.<sup>624b</sup>  
 1-Thiocyano-piperidino-, 5-, m. 164°; 8-, m. 164°.<sup>624b</sup>  
 1-Thiocyano-2-methyl-, m. 194°.<sup>624b</sup>

#### THIOCYANO-ACIDS

- Thiocynoacetic, NCSCH<sub>2</sub>COOH, m. 40–2°;<sup>1882</sup> 35–40°;<sup>567</sup>  
 Affinity constant,  $K=0.265$ ; <sup>1350</sup> dissociation constant  $K_{25}$   
 $2.65 \times 10^{-3}$ ; <sup>1350</sup>  $K=0.003$ ; rate of hydrolysis 0.00173/min; <sup>1882</sup>  
 N<sub>2</sub>H<sub>4</sub> salt, m. 87–90°;<sup>572</sup> Esters: Me,  $b_{18}$  120–2°;<sup>1875</sup> d 20/4  
 1.2510; n 20/D 1.4828; <sup>1721</sup> Et,  $b_5$  110–5°;<sup>1801</sup>  $b_{10}$  109–10°;<sup>603</sup>  
 115–25°; 117°,  $b_{15}$  118–22°;<sup>1875</sup>  $b_{17}$  121–1.5°;<sup>828a</sup> 121–2°;<sup>812</sup>  $b_{18}$   
 118–22°;<sup>1875</sup> b. 225°;<sup>1020</sup> 220°;<sup>772</sup> d 1.174<sup>772</sup>; <sup>1020</sup> d 20/4 1.175;<sup>828a</sup>  
 $i$ -Pr  $b_{23}$  131–2°; d 20/4 1.126; Bu,  $b_{23}$  148–9°; d 20/4 1.098;  
 $i$ -Bu,  $b_{20}$  143–4°; d 20/4 1.095;<sup>1694</sup> Am, d 20/4 1.0763; n 20/D  
 1.4689; <sup>1721</sup>  $i$ -Am, b. 255°;  $b_{17}$  145–7°;<sup>1875</sup>  $b_{20}$  154–7°;<sup>1694</sup> d 20/4  
 1.063; <sup>1694</sup> Hex,  $d_{15}$  1.0610; Hept,  $d_{15}$  1.0411; Oct,  $d_{15}$  1.0166;  
 Non,  $d_{15}$  1.0097; <sup>1077</sup> Dec, d 20/4 0.9947; n 20/D 1.4673; Dodec

- d 20/4 0.9776; n 20/D 1.4672; cyclohexyl, d 20/4 1.1148; n 20/D 1.4972; <sup>1721</sup> 4-*t*-Butylcyclohexyl, b. 133–6°; <sup>1806</sup> 2-Furyl, m. 53°; <sup>1694</sup> 2-Chloroethyl, b<sub>0.8</sub> 113–4°; d 20/4 1.354; <sup>1694</sup> CCl<sub>3</sub>CMe<sub>2</sub>-, m. 81°; <sup>1694</sup> NCCMe<sub>2</sub>-, b<sub>0.2</sub> 113°; <sup>349</sup> Phenyl, m. 28–32°; <sup>1877c</sup> d<sub>15</sub> 1.12165; <sup>1077</sup> *p*-Chlorophenyl, m. 66–7°; b<sub>2.5</sub> 171–2°; 2,4-Dichlorophenyl, m. 67°; b<sub>1</sub> 169–72°; <sup>1694</sup> Benzyl, d<sub>15</sub> 1.2170; 2-Phenethyl, d<sub>15</sub> 1.1619; <sup>1077</sup> 3-Phenylpropyl, d<sub>15</sub> 1.1231; β-Naphthyl, m. 95°; <sup>1077</sup> Phenylene, *o*-, m. 54°; <sup>1077</sup> *m*-, m. 54°; *p*-, m. 134°; <sup>1077</sup> Anilide, m. 94°; <sup>1877c</sup> 87°; <sup>124.5</sup> 86°; <sup>703</sup> Chloranilide, *m*-, m. 166°; <sup>124.5</sup> *p*-, m. 126°; <sup>124.5</sup> Nitroanilide, *o*-, m. 154°; <sup>124.5</sup> *m*-, m. 180°; <sup>124.5</sup> *p*-, m. 174°; <sup>124.5</sup> Anisidide, *o*-, m. 72°; <sup>124.5</sup> *p*-, m. 111°; <sup>124.5</sup> Phenetidide, m. 131°; <sup>124.5</sup> Toluide, *o*-, m. 109°; <sup>124.5</sup> 103°; <sup>703</sup> *m*-, m. 136°; <sup>124.5</sup> *p*-, m. 85°; <sup>1877c</sup> Me(NO<sub>2</sub>)C<sub>6</sub>H<sub>3</sub>NH-, 2,4-, m. 158°; <sup>124.5</sup> 4,3-, m. 184°; <sup>124.5</sup> 4,2-, m. 133°; <sup>124.5</sup> Xylide, *o*-, m. 111°; <sup>703</sup> 102°; <sup>703</sup> *m*-, m. 98°; <sup>922</sup> *p*-, m. 133°; <sup>703</sup> 2,4,5-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>NH-, 105°; <sup>124.5</sup> Methylanilide, m. 79°; <sup>124.5</sup>
- α-Thiocyanopropionic, MeCH(SCN)COOH, *DL*, m. 51°; <sup>567</sup> K<sub>25</sub>=3.62 × 10<sup>-3</sup>; <sup>567</sup> *L*-acid, m. 53°; [α] 25/D –55.0°; K salt, [α] 25/D –58.2° (H<sub>2</sub>O, C=5.4); <sup>567</sup> *D*-acid, m. 53°; [α] 25/D +54.2° (alc. C=3.3); <sup>567</sup> [α] +58.3°; <sup>567</sup> K salt [α] 25/D +58.3° (H<sub>2</sub>O, C=5.3); <sup>567</sup> Esters: Me, b<sub>15</sub> 104–6°; <sup>1875</sup> Et b<sub>16</sub> 107–8°; <sup>1875</sup> b<sub>20</sub> 119°; <sup>1875</sup> [α] 20/5790 –7.51°; n 20/D 1.4657; <sup>638</sup> *i*-Bu, b<sub>15</sub> 130–1°; <sup>1875</sup> *i*-Am, b<sub>15</sub> 141.5°; <sup>1875</sup>
- β-Thiocyanopropionic, NCSH<sub>2</sub>CH<sub>2</sub>COOH, m. 9.5°; <sup>674</sup> 8.5°; <sup>567</sup> K<sub>25</sub>=1.32 × 10<sup>-4</sup>; <sup>567</sup> Esters: Me, b<sub>0.3</sub> 73–6°; b<sub>0.5</sub> 78–80°; d 25/25 1.1839–40; n 25/D 1.4770–72; Et, b<sub>3</sub> 101–5°; b<sub>10</sub> 124°; d 20/25 1.1381, d 25/25 1.1281; n 20/D 1.4699, n 25/D 1.4678; <sup>1156</sup> Cyclohexyl, n 20/D 1.4940; <sup>837</sup> Dihydroisophoryl, b<sub>4.7</sub> 149–51°; <sup>1156</sup>
- α-Thiocyanobutyric, EtCH(SCN)COOH, Esters: Me, b<sub>23</sub> 125°; Et, b<sub>28</sub> 134–6°; *i*-Am, b<sub>19</sub> 110–3.5°, b<sub>23</sub> 158–60°; <sup>1875</sup>
- α-Thiocyano-*i*-butyric, Me<sub>2</sub>C(SCN)COOH, Esters: Me, b<sub>17</sub> 101–2°; Et, b<sub>22</sub> 111–5°; *i*-Bu, b<sub>21</sub> 132–3°; *i*-Am, b<sub>16</sub> 135.5–6.5°; <sup>1875</sup>
- α-Thiocyano-*i*-valeric, Me<sub>2</sub>CHCH(SCN)COOH, Esters: Me, b<sub>23</sub> 119–21.5°; d 20/15.6 1.1141; n 20/D 1.4693; <sup>1875</sup> Et, b<sub>19</sub> 126–8°; *i*-Bu, b<sub>19</sub> 145–7°; *i*-Am, b<sub>14</sub> 151–2°; <sup>1875</sup>
- 11-Thiocyanoundecanoic, NCSCH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>COOH, m. 52°; <sup>177</sup> NCSCHPhCOOH, amide, m. 143–5°; *DL*, Et ester, b<sub>17</sub> 182–4°; <sup>1874</sup>

- NCSCPh<sub>2</sub>COOCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>, m. 94–6°. <sup>1024</sup>
- Thiocyanomalonic, CH(SCN)(COOH)<sub>2</sub>, Et ester, b<sub>23</sub> 169–70°. <sup>1874</sup>
- Thiocyano-methyl malonic, CH<sub>3</sub>C(SCN)(COOH)<sub>2</sub>, Et ester, b<sub>9</sub> 139–42°. <sup>1877c</sup>
- 6-Hydroxy-8-thiocyano-octanoic, NCSCH<sub>2</sub>CH<sub>2</sub>CHOH(CH<sub>2</sub>)<sub>4</sub>-COOH, Esters: Me n 25/D 1.4940, 0.0040; Et, b<sub>1.0</sub> 200–5°; n 25/D 1.4860. <sup>887</sup>
- 4-Thiocyano-2-acetyl-butyrlic, NCSCH<sub>2</sub>CH(COMe)COOH, Et ester, m. 83°. <sup>1035</sup>
- NCSCH<sub>2</sub>COCH(CN)COOEt, m. 82–4°. <sup>137</sup>
- o*-NCSC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>COOH, m. 104°. <sup>1491.5</sup>
- Thiocyanoglycino, NCSCH(NH<sub>2</sub>)COOH, [α] 18/D –83.17°. <sup>1212</sup>
- H<sub>2</sub>NCH<sub>2</sub>CH(SCN)COOEt, Phthalimid, m. 83–5°.
- Thiocyanobenzoic, NCSC<sub>6</sub>H<sub>4</sub>COOH, *o*-, m. 166°; Me ester, m. 77°; <sup>152</sup> *p*-, m. 210°. <sup>200</sup>
- NCSC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>COOH, *o*-, m. 106°. <sup>1194</sup>
- NCSC<sub>6</sub>H<sub>4</sub>CH:CHCOOH, *o*-, m. 175°. <sup>344</sup>
- NCSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>COOH, *o*-, m. 70°; *p*-, m. 159°. <sup>633</sup>
- Thiocyanosalicylic, 2,*x*-HO(NCS)C<sub>6</sub>H<sub>3</sub>COOH, 4-, m. 195–7°. <sup>1780</sup>
- Thiocyanoanthranilic, 2,4-H<sub>2</sub>N(NCS)C<sub>6</sub>H<sub>3</sub>COOH, 4-, O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CO-, *o*-, m. 129°; *m*-, m. 164°; *p*-, m. 189°; PhNHCO-, m. 173°; *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NHCO-, m. 156°; <sup>947</sup> 170°; <sup>1400</sup> Esters: Me, m. 113°. <sup>1316.5</sup>
- 2,4-NCS(AcNH)C<sub>6</sub>H<sub>3</sub>CH:CHCOOH, m. 208°. <sup>1491.6</sup>
- 5-Thiocyano-5-carboxy-anthraquinone, m. 302°. <sup>624c</sup>

## BIS- AND TRIS-THIOCYANATES

- Methylene, CH<sub>2</sub>(SCN)<sub>2</sub>, m. 105.4°, <sup>1486</sup> 102°. <sup>1110</sup>
- Ethylene, (·CH<sub>2</sub>SCN)<sub>2</sub>, m. 90.5°, <sup>422, 1486</sup> 90°, <sup>268a, 857, 958, 959, 960, 974, 1110, 1684, 1690</sup> 88°. <sup>1049</sup>
- MeCH(SCN)CH<sub>2</sub>SCN, oil. <sup>422, 1728</sup>
- MeCH(SCN)CHMe(SCN), b<sub>6</sub> 150°. <sup>1128</sup>
- EtCH(SCN)CH<sub>2</sub>SCN, b<sub>18</sub> 178°; d 20/4 1.194. <sup>414a</sup>
- MeCH(SCN)CMe<sub>2</sub>(SCN), b<sub>6</sub> 65–70°. <sup>289a</sup>
- Me<sub>2</sub>C(SCN)CMe<sub>2</sub>(SCN), m. 61°. <sup>1928</sup>
- Trimethylene, CH<sub>2</sub>(CH<sub>2</sub>SCN)<sub>2</sub>, m. 23°, <sup>1728</sup> 22.4°, <sup>1486</sup> 17.5°; <sup>779a</sup> b<sub>0.05</sub> 129–30°. <sup>1498</sup>
- Tetramethylene, (·CH<sub>2</sub>CH<sub>2</sub>SCN)<sub>2</sub>, b<sub>11</sub> 202–4°, <sup>1498</sup> b<sub>14</sub> 193–5°. <sup>228</sup>
- Pentamethylene, CH<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>SCN)<sub>2</sub>, b<sub>2</sub> 210–11.5°, <sup>1498</sup> b<sub>11</sub> 221–2°. <sup>234</sup>

- $\text{NCSCH:CHSCN}$ , *cis*, m. 15–17°; d 16.5–4 1.332; <sup>1684, 1685</sup> *trans*, m. 97–98.5°, <sup>1684, 1685</sup> 97°. <sup>1323</sup>  
 $\text{NCSCH}_2\text{CH:CHCH}_2\text{SCN}$ , 83.5°, <sup>1277</sup> 82°. <sup>278</sup>  
 $\text{NCSCH}_2\text{CMe:CHCH}_2\text{SCN}$ , m. 77°. <sup>262</sup>  
 $\text{NCSCH}_2\text{CMe:CMeCH}_2\text{SCN}$ , m. 130°. <sup>262</sup>  
 1,2-Dithiocyanocyclohexane, m. 58.5°. <sup>422</sup>  
 Methyl-1,2-dithiocyanocyclohexane, 2-, m. 60°; <sup>1271a, 1273</sup> 3-, m. 70°; <sup>422</sup> 4-, m. 81°; <sup>1273, 1271a</sup>  $[\alpha]_{579}$  19.2°;  $[\alpha]_{546}$  22.3°. <sup>1273</sup>  
 2-Ethyl-1,2-dithiocyanocyclohexane, m. 83°; <sup>1273</sup> 82°. <sup>1271a</sup>  
 2-Propyl-1,2-dithiocyanocyclohexane, m. 87°; <sup>1273</sup> 86°. <sup>1271a</sup>  
 1-Thiocyano-1-thiocyanomethylcyclohexane, m. 63°. <sup>1273</sup>  
 $\text{NCSCHBrCHBrSCN}$ , *cis*, m. 84°; *trans*, m. 111°. <sup>1684, 1685</sup>  
 $\text{NCSCH}_2\text{CHBrCHBrCH}_2\text{SCN}$ , m. 142°. <sup>1277</sup>  
 $\text{O}(\text{CH}_2\text{SCN})_2$ , m. 18.5°;  $b_{2.5-3}$  101.5–2°; d 20/4 1.3153; n 20/D 1.6117. <sup>783</sup>  
 $\text{O}(\text{CH}_2\text{CH}_2\text{SCN})$ , d 20/4 1.2465. <sup>1912.5</sup>  
 $\text{OC}(\text{CH}_2\text{CMe}_2\text{SCN})_2$ ,  $b_{1-2}$  150–5°. <sup>259a</sup>  
 $\text{MeN}(\text{CH}_2\text{CH}_2\text{SCN})_2$ , HCl, m. 115–7°; picrate, m. 176°. <sup>879</sup>  
 $(\cdot\text{NHC:CMe}_2\text{SCN})_2$ , m. 150°. <sup>334</sup>  
 $(\cdot\text{NHC:C}(\text{CH}_2\text{CH}_2)_2\text{CH}_2\text{SCN})_2$ , m. 181°. <sup>334</sup>  
 $(\cdot\text{N:CMeCH}_2\text{SCN})_2$ , m. 112–14°. <sup>151.5</sup>  
 $\text{NCSCH}_2\text{CH}_2\text{CH}(\text{SCN})(\text{CH}_2)_4\text{COOEt}$ , n 25/D 1.5081. <sup>837</sup>  
 $\text{Me}(\text{CH}_2)_4\text{CHXCHXCH}_2\text{CH}(\text{SCN})\text{CH}(\text{SCN})(\text{CH}_2)_7\text{COOH}$ ,  
 $\text{X}=\text{Cl}$  d 35/4 1.511;  $=\text{Br}$ , d 35/4 1.2802;  $=\text{Cl}$ , I, d 35/4 1.2559;  $=\text{Br}$ , I d 35/4 1.3587. <sup>1001b</sup>  
 $\text{PhCH}(\text{SCN})\text{CH}_2\text{SCN}$ , m. 101°. <sup>972a, 974</sup>  
 $\text{PhCH}(\text{SCN})\text{CHPh}(\text{SCN})$ , m. 226°. <sup>1684, 1685</sup>  
 $\text{PhC}(\text{SCN})\text{:CH}(\text{SCN})$ , m. 68°. <sup>1684, 1685</sup>  
 $\text{PhC}(\text{SCN})\text{:CPh}(\text{SCN})$ , m. 195°. <sup>1684, 1685</sup>  
 $\beta\text{-C}_{10}\text{H}_7\text{CH}(\text{SCN})\text{CH}_2\text{SCN}$ , m. 130.5°. <sup>1701</sup>  
 2-Thienyl  $\text{CHSCNCH}_2\text{SCN}$ , m. 87°. <sup>499.5</sup>  
 5-Chloro-2-thienyl  $\text{CHSCNCH}_2\text{SCN}$ , m. 98°. <sup>499.5</sup>  
 5-Bromo-2-thienyl  $\text{CHSCNCH}_2\text{SCN}$ , m. 96°. <sup>499.5</sup>  
 2,5-Dithiocyano-3,4-dinitrothiophene, dec. 240°. <sup>1164</sup>  
 Phenylene,  $\text{C}_6\text{H}_4(\text{SCN})_2$ , *m*-, m. 54°; <sup>606a</sup> *p*-, m. 108.5°, <sup>434a</sup> 106°. <sup>321</sup>  
 1,4-Dithiocyano-nitrobenzene, 2-, m. 144°; <sup>905.5</sup> 3-, m. 143°. <sup>905.5</sup>  
 1,3-Dithiocyano-4,6-dinitrobenzene, m. 200°. <sup>812</sup>  
 $(\text{NCS})_2\text{C}_6\text{H}_3\text{COMe}$ , 2,5-, m. 118°; 3,4-, m. 93.5°. <sup>285</sup>  
 3,5-Dithiocyanosulfanilamide, m. 270°. <sup>350</sup>

- Xylene,  $\text{C}_6\text{H}_4(\text{CH}_2\text{SCN})_2$ , *o*-, m.  $79^\circ$ ; <sup>1726b</sup> *m*-, m.  $62^\circ$ , <sup>731</sup> *p*-, m.  $134^\circ$ . <sup>1726b</sup>
- Me(NCSC $\text{H}_2$ ) $_2$ C $_6$ H $_2$ OH, 2,4,6-, m.  $116^\circ$ ; <sup>1379.5</sup> 4,2,6-, m.  $214^\circ$ . <sup>1945</sup>
- 2,5,1,4-Cl $_2$ C $_6$ H $_2$ (OCH $_2$ SCN) $_2$ , m.  $174^\circ$ . <sup>96</sup>
- p*-CCl $_3$ CH(C $_6$ H $_4$ SCN) $_2$ , m.  $230^\circ$  dec. <sup>349.5</sup>
- 4,4'-HN(C $_6$ H $_4$ SCN) $_2$ , m.  $120^\circ$ . <sup>1685</sup>
- 4,4'-PhN(C $_6$ H $_4$ SCN) $_2$ , m.  $116^\circ$ . <sup>1685</sup>
- [C $_6$ H $_3$ (NO $_2$ )SCN-3,4] $_2$ , m.  $307^\circ$ . <sup>810</sup>
- 7,2,4-HOC $_{10}$ H $_5$ (SCN) $_2$ , m.  $119^\circ$ . <sup>974</sup>
- 7,2,4-H $_2$ NC $_{10}$ H $_5$ (SCN) $_2$ , m. about  $200^\circ$  dec. <sup>1254.5</sup>
- 1,4-Dihydronaphthalene dithiocyanate, m.  $113^\circ$ . <sup>1271a</sup>
- Dithiocyano-1,2,3,4-tetrahydronaphthalene, 1,2-, m.  $80^\circ$ ; <sup>1701</sup>
- 2,3-, m.  $117-20^\circ$ . <sup>1701</sup>
- 2,3-Dithiocyano-1,4-naphthoquinone, m.  $235-40^\circ$ . <sup>1562</sup>
- 2,3-Dithiocyano-5-nitro-1,4-naphthoquinone, m.  $> 270^\circ$ . <sup>1562</sup>
- 2,3-Dithiocyanomethyl-1,4-naphthoquinone, m.  $180^\circ$ . <sup>1562</sup>
- 9,9-*bis*-(Thiocyano)fluorene, m.  $144^\circ$ . <sup>782</sup>
- 3,3-*bis*-(Thiocyanomethyl)oxetane, m.  $82.1^\circ$ .
- $\alpha,\alpha'$ -Dithiocyanopyrrole, m.  $114^\circ$ . <sup>1683.5</sup>
- N-Methyl-dithiocyanopyrrole, m.  $119^\circ$ . <sup>1683.5</sup>
- 1,4-Dimethyl-1,4-(di- $\beta$ -Thiocyanoethyl)piperazinium dithiocyanate, m.  $180^\circ$  dec. <sup>879</sup>
- NCSCH(CH $_2$ )(SCN) $_2$ , m.  $126^\circ$ . <sup>779a</sup>
- N(CH $_2$ CH $_2$ SCN) $_3$ , m.  $147^\circ$ . <sup>1327</sup>

## SELENOCYANATES

- Ethyl, EtSeCN,  $b_{741}$   $172^\circ$ . <sup>1878</sup>
- Butyl, BuSeCN,  $b_{13}$   $88-90^\circ$ . <sup>1857</sup>
- s*-Butyl, MeCH $_2$ CHMeSeCN,  $b_{16}$   $83^\circ$ ;  $d_{20/4}$  1.445;  $n_{19/D}$  1.4965;  $[\alpha]_{5461}$   $13.9^\circ$ . <sup>991</sup>
- t*-Butyl, Me $_3$ CSeCN,  $b_{0.6}$   $65^\circ$ . <sup>243</sup>
- Hexyl, C $_6$ H $_{13}$ SeCN,  $b_{13}$   $114^\circ$ . <sup>1857</sup>
- Decyl, C $_{10}$ H $_{21}$ SeCN,  $b_{0.2}$   $97-8^\circ$ . <sup>1857</sup>
- Allyl, CH $_2$ :CHCH $_2$ SeCN,  $b_{0.12}$   $75^\circ$ . <sup>243</sup>
- ClCH $_2$ CH $_2$ SeCN,  $b_{0.6}$   $91^\circ$ . <sup>243</sup>
- Cl $_2$ CHCH $_2$ SeCN, m.  $81^\circ$ ;  $b_4$   $99-100^\circ$ . <sup>243</sup>
- ClCH $_2$ CH $_2$ CH $_2$ SeCN,  $b_{0.8}$   $96^\circ$ . <sup>243</sup>
- CHCl:CClSeCN, m.  $65^\circ$ . <sup>243</sup>
- CH $_2$ :CBrCH $_2$ SeCN,  $b_{0.2}$   $88^\circ$ . <sup>243</sup>
- (MeCO) $_2$ CHSeCN, m.  $80^\circ$ . <sup>1263</sup>

- EtCOCH(SeCN)COMe, m. 27.5°. <sup>1264</sup>
- Phenyl, PhSeCN, b<sub>10</sub> 134°, <sup>321</sup> b<sub>11</sub> 117–8°, b<sub>16</sub> 125°, b<sub>17</sub> 127°, <sup>127a, b</sup> b. 250°. <sup>321</sup>
- ClC<sub>6</sub>H<sub>4</sub>SeCN, *o*-, m. 45°; b<sub>20</sub> 152–3°; <sup>127b</sup> *p*-, m. 54.5°, <sup>127b</sup> 53°; <sup>322</sup> d 57.5/4 1.590, d 89/4 1.557; surface tension, 43.02 dyn/cm at 58°, 40.03 dyn/cm at 85.5°. <sup>777</sup>
- p*-BrC<sub>6</sub>H<sub>4</sub>SeCN, m. 71.5°; <sup>777</sup> d 75.5/4 1.842, d 86/4 1.814; surface tension 43.6 dyn/cm at 76°, 41.6 dyn/cm at 91.0°. <sup>777</sup>
- O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SeCN, *o*-, m. 145°, <sup>808</sup> 143°, <sup>321</sup> 142°; <sup>812</sup> *m*-, m. 65°; <sup>321</sup> *p*-, m. 141°, <sup>321</sup> 139.4°, <sup>1649</sup> 138°, <sup>289</sup> 135°. <sup>112</sup>
- 2,4-(O<sub>2</sub>N)ClC<sub>6</sub>H<sub>3</sub>SeCN, m. 127°. <sup>321</sup>
- 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SeCN, m. 163°. <sup>592</sup>
- p*-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SeCN, m. 93.5°, <sup>130</sup> 92°. <sup>289</sup>
- p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SeCN, m. 105°. <sup>289</sup>
- p*-AcOC<sub>6</sub>H<sub>4</sub>SeCN, m. 67°. <sup>989.5</sup>
- p*-MeOC<sub>6</sub>H<sub>4</sub>SeCN, 65°. <sup>289</sup>
- p*-NCSC<sub>6</sub>H<sub>4</sub>SeCN, m. 112°, <sup>289</sup> 110°. <sup>321</sup>
- 2,4-O<sub>2</sub>N(NCS)C<sub>6</sub>H<sub>3</sub>SeCN, m. 147°. <sup>321</sup>
- Benzyl, PhCH<sub>2</sub>SeCN, m. 72°, <sup>1477a, b</sup> 71.5°. <sup>887</sup>
- O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SeCN, *o*-, m. 77°; <sup>592</sup> *p*-, m. 122.5°. <sup>887</sup>
- NCC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SeCN, *o*-, m. 121°; <sup>455</sup> *m*-, m. 55°; <sup>489</sup> *p*-, m. 86°. <sup>1269</sup>
- Tolyl, MeC<sub>6</sub>H<sub>4</sub>SeCN, *o*-, b<sub>20</sub> 135°, b<sub>30</sub> 154–5°; <sup>126</sup> *p*-, m. 56°. <sup>332</sup>
- (O<sub>2</sub>N)MeC<sub>6</sub>H<sub>3</sub>SeCN, 2,4-, m. 150°; <sup>910</sup> 3,4-, m. 70°. <sup>910</sup>
- Triphenylmethyl, Ph<sub>3</sub>CSeCN, m. 130.5°. <sup>1486</sup>
- β-Naphthyl, m. 68°, <sup>1141</sup> 63.9°. <sup>1477a, b</sup>
- PhCOCH<sub>2</sub>SeCN, m. 85°. <sup>820</sup>
- 1-Selenocyanoanthroquinone, m. 249°. <sup>117a</sup>
- 1,4-Methoxyanthraquinoneselenocyanate, m. 264°. <sup>905</sup>
- H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>SeCN, phthalimid, m. 125°. <sup>359</sup>
- H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SeCN, phthalimid, m. 102°. <sup>359</sup>
- NCSCH<sub>2</sub>COOH, m. 85°; <sup>820, 561</sup> K=1.79 × 10<sup>-3</sup>; <sup>567</sup> amide, m. 124°; anilide, m. 129°; chloranilide, *m*-, m. 118°; *p*-, m. 178°; bromanilide, *m*-, m. 105°; *p*-, m. 188°; Methyl phenyl amide, m. 78°; Diphenylamide, m. 103°; Phenyl benzyl amide, m. 70°; Toluide, *o*-, m. 126°; *m*-, m. 136°; *p*-, m. 160°; xylide, *m*-, m. 148°; *p*-, m. 144–6°; <sup>573</sup> ureide, m. 179°. <sup>573</sup>
- MeCH(SeCN)COOH, *DL*, m. 70°, K=2.81 × 10<sup>-3</sup> at 25°; <sup>567</sup> ureide m. 136°; *L* m. 91°, [α] 25/D -11.2 (H<sub>2</sub>O C=3.7), -14.2 (H<sub>2</sub>O C=1.9), -58.1 (alc.c=3.8), -33.8 (acetone C=3.7), -51.7 (HOAc C=3.7); K salt [α] 25/D -67.1

(H<sub>2</sub>O) <sup>567</sup> Et ester, b<sub>0.1</sub> 63–4°; [α] 17.5/5461 –0.91°.<sup>638</sup>  
 NCSeCH<sub>2</sub>CH<sub>2</sub>COOH, m. 58°; K=1.40 × 10<sup>–4</sup> at 25°.<sup>567</sup>  
 EtCH(SeCN)COOH, m. 51°; K=2.70 × 10<sup>–3</sup> at 25°.<sup>567</sup>  
 Me<sub>2</sub>C(SeCN)COOH, m. 80°; K=6.1 × 10<sup>–3</sup> at 25°.<sup>567</sup>  
 Me<sub>2</sub>CHCH(SeCN)COOH, m. 109°.<sup>568</sup>  
 o-NCSeC<sub>6</sub>H<sub>4</sub>COOH, m. 185°; Esters: Me, m. 115°; Et, m. 126°;  
 chloride, m. 123°.<sup>1111</sup>

### BIS-SELENOCYANATES

CH<sub>2</sub>(SeCN)<sub>2</sub>, m. 139.3°,<sup>1477a, b</sup> 132°.<sup>1447</sup>  
 (·CH<sub>2</sub>SeCN)<sub>2</sub>, m. 138°,<sup>728</sup> 137.8°,<sup>1477a, b</sup> 128°.<sup>1447</sup>  
 MeCH(SeCN)CH<sub>2</sub>SeCN, m. 66°.<sup>728</sup>  
 CH<sub>2</sub>(CH<sub>2</sub>SeCN)<sub>2</sub>, m. 51°,<sup>728</sup> 50.6°.<sup>1477a, b</sup>  
 (·CH<sub>2</sub>CH<sub>2</sub>SeCN), m. 40°.<sup>1263</sup>  
 CH<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>SeCN), oil.<sup>1263</sup>  
 1,4-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SeCN)<sub>2</sub>, m. 154°.<sup>243</sup>

### Properties of Isothiocyanates

#### ALKYL ISOTHIOCYANATES

Methyl, CH<sub>3</sub>NCS, m. 35.93°,<sup>647a</sup> 35°,<sup>150b, 946, 1301</sup> 34°,<sup>813, 814 1069</sup>  
 b<sub>759</sub> 119°,<sup>1301</sup> b<sub>758</sub> 117°,<sup>1847</sup> 116°,<sup>1207</sup> b<sub>756</sub> 117.5° cor.,<sup>473, 946</sup> b<sub>750</sub>  
 119°,<sup>412d, 813, 814, 1301, 1678</sup> 118°;<sup>473, 946</sup> d 37.2/4 1.06912; n 37.2/D  
 1.52576,<sup>412d 1301</sup> n 40/D 1.5245; heat of fusion 2029.5 cal.;<sup>647a</sup>  
 Molecular heat of combustion (gas) 392.06 cal at constant  
 pressure;<sup>1775</sup> (solid) 441.6 cal at constant volume, 442.6 cal at  
 constant pressure;<sup>150b</sup> heat of formation –9.4 cal;<sup>150b</sup> dielec-  
 tric constant at 40° 17.9,<sup>486</sup> at 38° 20.3,<sup>1207</sup> at 37° 19.7,<sup>1847</sup> at  
 20° 17.9–19.7.<sup>1847</sup>  
 Ethyl, CH<sub>3</sub>CH<sub>2</sub>NCS, m. –5.9°;<sup>1590</sup> b<sub>10</sub> 4.9°, b<sub>20</sub> 8.7°, b<sub>30</sub> 15.0°,  
 b<sub>40</sub> 24.4°,<sup>113</sup> b<sub>50</sub> 39.1°,<sup>113</sup> b<sub>120</sub> 60–70°,<sup>987</sup> b<sub>760</sub> 131–1.5°,<sup>1847</sup> b<sub>758</sub>  
 131–2.1°,<sup>1301</sup> b<sub>756</sub> 131.5–2°,<sup>1506</sup> b. 134°,<sup>813, 814</sup> 133.2°,<sup>268a</sup>  
 133°,<sup>1242, 1477a</sup> 132°, 131.2°,<sup>486</sup> 131°;<sup>1308</sup> d 0/4 1.0194,<sup>412d</sup>  
 1.01911,<sup>268d</sup> d<sub>0</sub> 1.0192,<sup>268c</sup> d 15.4/4 1.0035,<sup>765</sup> d<sub>16.5</sub> 1.0030,<sup>655</sup> d<sub>18</sub>  
 1.0030,<sup>655</sup> d 18.4 1.001,<sup>1468</sup> d<sub>20</sub> 0.998,<sup>1847</sup> d 20/4 0.9990,<sup>850</sup> d  
 21.4/4 0.9975,<sup>268a</sup> d<sub>22</sub> 0.9972,<sup>268c</sup> d 23.4/4 0.99525,<sup>412d, 1301</sup> d 25/4  
 0.9938,<sup>1847</sup> d 30/4 0.9888,<sup>1265</sup> d<sub>46</sub> 0.972,<sup>1468</sup> d 50/4 0.9672,<sup>1071</sup>  
 d 133.2/4 0.8735,<sup>268a</sup> 0.8763;<sup>268c</sup> n 20/D 1.5130,<sup>850</sup> n 23.4/D  
 1.51093;<sup>412d, 1301</sup> surface tension 35.02 dyn/cm at 18.4°, 31.49  
 dyn/cm at 46°;<sup>1468</sup> free surface energy 74.2;<sup>748</sup> viscosity at  
 50° 0.00480;<sup>1468</sup> critical temperature 356.7°;<sup>1468</sup> specific con-



- ductivity  $2.25 \times 10^{-5}$ ; <sup>207</sup> dielectric constant 23.4 at 2°, 22.0 at 15°, <sup>486, 937</sup> 18.7 at 18°, <sup>1207</sup> 19.4–22.0 at 20°, 19.5 at 21°; <sup>1847</sup> heat of formation –7.6 cal; <sup>150b</sup> Molecular heat of combustion, 602.8 cal at constant volume, 604.1 cal at constant pressure. <sup>150a</sup>
- Propyl,  $C_3H_7NCS$ ,  $b_{743}$  152.7°, <sup>769a</sup> b. 154–5°, <sup>1424b</sup> 153° cor.; <sup>173</sup> d 0/4 0.9907, <sup>769a</sup> d 16/4 0.9781, <sup>412d</sup> d 99.4/0 0.9304; <sup>769a</sup> n 16/D 1.5085. <sup>412d</sup>
- i*-Propyl,  $Me_2CHNCS$ ,  $b_{10}$  29–30°;  $b_{11}$  35–40°, <sup>522</sup> b. 138°, <sup>533</sup> 137–7.5, <sup>897b</sup> 137°, <sup>1477b</sup> 134–40°; <sup>222a, d</sup> d 20/4 0.9475; n 20/D 1.4734, <sup>1585</sup> 1.4934. <sup>1585</sup>
- Butyl,  $C_4H_9NCS$ ,  $b_9$  58.4°, <sup>1585</sup> 58.9°, <sup>1585</sup> 58–9°, <sup>522</sup>  $b_{32}$  83.5°, <sup>809</sup> b. 166° cor., <sup>473</sup> 167°, <sup>813, 814</sup>  $b_{724}$  164.6–5.3°; <sup>195</sup>  $d_{11.2}$  0.9559,  $d_{14.9}$  0.9519, <sup>195</sup> d 20/4 0.9546, <sup>1585</sup>  $d_{22}$  0.9452,  $d_{30.8}$  0.9367,  $d_{55.2}$  0.9140,  $d_{80.6}$  0.8890,  $d_{108}$  0.8626; <sup>195</sup> n 20/D 1.501; <sup>1585</sup> surface tension 31.34 at 11.2°, 26.83 at 55.2°, 21.57 at 108.5°; <sup>195</sup> surface energy 62.4. <sup>748</sup>
- i*-Butyl,  $Me_2CHCH_2NCS$ ,  $b_{29}$  72.5°, <sup>809</sup> b. 160° cor., <sup>412d</sup> 162°, <sup>813, 814, 1460</sup> 161–3°, <sup>813, 814, 817</sup> 165–70°; <sup>1424b</sup> d 14/2 0.9638; <sup>412d</sup> n 14/D 1.5005. <sup>412d</sup>
- s*-Butyl,  $EtCH(Me)NCS$ , *DL* b. 159.5°;  $d_{12}$  0.944; <sup>813, 814</sup> *D* b. 159°, <sup>1772</sup> 150–6°, <sup>813, 814</sup> 159–63°; d 20/4 0.943;  $[\alpha]$  20/D + 61.88, <sup>1772</sup> natural + 55.27, synthetic + 61.36, <sup>615b</sup> in 16% soln in 94% alc. 66.22°; <sup>615f</sup> *L* b. 159°; d 20/4 0.942;  $[\alpha]$  20/D –61.80°. <sup>1772</sup>
- t*-Butyl,  $Me_3CNCS$ , m. 11.5°, 10.5°; <sup>1531a, b, c, d, e</sup>  $b_{10}$  30.5–2°, <sup>1584</sup>  $b_{52}$  64°, <sup>208</sup> b. 142°, <sup>1531a, c</sup>  $b_{773}$  142.5°, <sup>1531b</sup>  $b_{770}$  140°; <sup>1531d, e</sup>  $d_{15}$  0.9187, <sup>1531b, d, e</sup>  $d_{34}$  0.9003; <sup>1531b, d, e</sup> n 25/D 1.4780.
- Amyl,  $C_5H_{11}NCS$ , b. 193.4° cor., <sup>946</sup> 191° cor. <sup>473</sup>
- i*-Amyl,  $Me_2CHCH_2CH_2NCS$ , b. 183° cor., <sup>473</sup> 184°, <sup>222a, d</sup> 183–4°, <sup>813, 814</sup> 182–5°, <sup>1713</sup> 182°, <sup>268a</sup> 180°, <sup>813, 814</sup> 188–9°; <sup>1424b</sup> d 0/0 0.957538, <sup>268a</sup>  $d_{17}$  0.94189,  $d_{182}$  0.78749. <sup>268a</sup>
- t*-Amyl,  $EtMe_2CNCS$ , liquid at –10°; <sup>1156</sup>  $b_{13}$  67–72°, <sup>1156</sup>  $b_{770}$  166°, <sup>1531b, d, e</sup> 164–7°; <sup>453</sup> d 20/25 0.9198; n 20/D 1.4820. <sup>1156</sup>
- Hexyl,  $C_6H_{13}NCS$ , b. 210° cor., <sup>473</sup>  $b_{758}$  212°, <sup>569, 1477b</sup>
- i*-Hexyl,  $Me_2CHCH_2CH_2CH_2NCS$ ,  $b_{18}$  120°, b. 208–9°. <sup>946</sup>
- s*-Hexyl,  $BuCH(Me)NCS$ , b. 197–8°; <sup>1813</sup>  $d_0$  0.9253. <sup>1813</sup>
- Heptyl,  $C_7H_{15}NCS$ , b. 241° cor., <sup>473</sup>  $b_{733}$  238°. <sup>1424b</sup>
- 2-Methylhexyl,  $BuCHMeCH_2NCS$ ,  $b_{769}$  228–9°. <sup>1671</sup>
- s*-Octyl,  $C_8H_{17}CH(Me)NCS$ , b. 234°, <sup>897a, b</sup> 232–2.5°. <sup>897b</sup>
- t*-Octyl,  $b_{2.5}$  67°,  $b_{28}$  108–12°. <sup>208</sup>

- $\text{Me}_2\text{CCH}_2\text{CMe}_2\text{NCS}$ ,  $b_{12}$   $83-5^\circ$ ,  $b_{28}$   $108-12$ ;  $d$  25/25 0.9043-5;  $n$  25/D 1.4811.<sup>1156</sup>  
*i*-Undecyl,  $\text{Me}_2\text{CH}(\text{CH}_2)_7\text{NCS}$ ,  $b_{17}$   $163-4^\circ$ .<sup>1424b</sup>  
*s*-Undecyl,  $\text{NonCH}(\text{Me})\text{NCS}$ ,  $b_{17}$   $163-4^\circ$ .<sup>1424</sup>  
 Dodecyl,  $\text{C}_{12}\text{H}_{25}\text{NCS}$ ,  $b_2$   $143-5^\circ$ .<sup>1623a</sup>  
 Pentadecyl,  $\text{C}_{15}\text{H}_{31}\text{NCS}$ , liquid.<sup>904</sup>  
 Cetyl,  $\text{C}_{16}\text{H}_{33}\text{NCS}$ ,  $b_{0.35}$   $180-94^\circ$ ;  $n$  20/D 1.4810.<sup>1843</sup>  
 Heptadecyl,  $\text{C}_{17}\text{H}_{35}\text{NCS}$ ,  $m$ .  $32^\circ$ .<sup>1805</sup>  
*c*-Pentyl,  $\text{C}_5\text{H}_9\text{NCS}$ ,  $b_{14}$   $80^\circ$ .<sup>227</sup>  
 1-Methyl-*c*-pentyl,  $\text{MeC}_5\text{H}_8\text{NCS}$ ,  $b_{30}$   $99-101^\circ$ ;  $d$  1.005;  $n$  1.5200.<sup>1159</sup>  
*c*-Hexyl,  $\text{C}_6\text{H}_{11}\text{NCS}$ ,  $b_9$   $94-5^\circ$ ,<sup>522</sup>  $b_{11-12}$   $97-8^\circ$ ,<sup>179</sup>  $b_{746}$   $219^\circ$ ,<sup>1672</sup>  $b_{749}$   $222^\circ$ ; <sup>1672</sup>  $d$  20/4 1.0339,<sup>1585</sup>  $d_{20}$  1.501,<sup>1585</sup>  $n$  20/D 1.5381,<sup>1585</sup> 1.538.<sup>1585</sup>  
 Methyl-*c*-hexyl,  $\text{MeC}_6\text{H}_{10}\text{NCS}$ ,  $b_{13}$   $115.5^\circ$ .<sup>232</sup>  
 Hexahydrobenzyl,  $\text{C}_6\text{H}_{11}\text{CH}_2\text{NCS}$ ,  $b_{17}$   $123-6^\circ$ .<sup>182.5</sup>  
 2-Isothiocyanoisocamphane,  $m$ .  $84-6^\circ$ .<sup>1157</sup>  
 Camphyl,  $b_{25}$   $160^\circ$ .<sup>232</sup>  
 Menthyl,  $b_{12}$   $138^\circ$ .<sup>232</sup>  
 Pinyll,  $b_{14}$   $142-3^\circ$ .<sup>232</sup>  
 Thujyl,  $b_{14}$   $126-8^\circ$ .<sup>232</sup>  
 Dihydronordicyclopentadienylisothiocyanate,  $b_6$   $140-2^\circ$ ;  $d$  25/4 1.1318.<sup>265</sup>

#### UNSATURATED ISOTHIOCYANATES

- Vinyl,  $\text{CH}_2:\text{CHNCS}$ ,  $b_{100}$   $46^\circ$ ,  $b_{150}$   $54^\circ$ ;  $d$  25/4 1.018;  $n$  35/D 1.505.<sup>931.5</sup>  
 Allyl,  $\text{CH}_2:\text{CHCH}_2\text{NCS}$ ,  $m$ .  $-102.5^\circ$ ,<sup>1782</sup>  $-100^\circ$ ; <sup>1781</sup>  $-80^\circ$ ; <sup>1782</sup>  $b_{760}$   $152.05^\circ$ ,<sup>782</sup>  $150.7^\circ$ ,<sup>1301</sup>  $148.2^\circ$ ,<sup>936a</sup>  $b_5$   $31.4^\circ$ ,<sup>936a</sup>  $30.65^\circ$ ,  $b_{10}$   $41.6^\circ$ ,<sup>1477b</sup>  $41.5^\circ$ ,<sup>936a</sup>  $b_{12}$   $44.5^\circ$ ,<sup>937</sup>  $b_{14}$   $47.17^\circ$ ,  $b_{15}$   $48.41^\circ$ ,  $b_{16}$   $49.73^\circ$ ,<sup>1477a</sup>  $b_{20}$   $53.8^\circ$ ,<sup>936a</sup>  $54.1^\circ$ ,<sup>1477b</sup>  $b_{22}$   $55.8^\circ$ ,<sup>936a</sup>  $b_{25}$   $57.8^\circ$ ,<sup>936a</sup>  $b_{29}$   $61.1^\circ$ ,<sup>936a</sup>  $b_{30}$   $61.7^\circ$ ,<sup>1477b</sup>  $b_{37}$   $66.3^\circ$ ,<sup>936a</sup>  $b_{50}$   $72.2^\circ$ ,<sup>936a</sup>  $73.1^\circ$ ,<sup>1477b</sup>  $b_{75}$   $81.2^\circ$ ,<sup>936a</sup>  $b_{93}$   $85.2^\circ$ ,<sup>437a</sup>  $b_{100}$   $89^\circ$ ,<sup>1477b</sup>  $b_{300}$   $119.5^\circ$ ,<sup>1477b</sup>  $b_{729}$   $150.4-0.7^\circ$ ,<sup>1041</sup>  $150.7^\circ$ ,<sup>1041</sup>  $b_{738}$   $150.0^\circ$ ,<sup>937</sup>  $b_{755}$   $151.8-2.2^\circ$ ,<sup>39</sup>  $158.8^\circ$ ,<sup>1071</sup>  $b_{759}$   $150.07^\circ$ ,<sup>1301</sup>  $b_{764}$   $150.5-0.9^\circ$ ,<sup>850</sup>  $150.7^\circ$ ,<sup>1301</sup>  $151.3^\circ$ ,<sup>1571b</sup>  $b$ .  $151.9^\circ$ ,<sup>1781</sup>  $161^\circ$ ,<sup>637</sup>  $151^\circ$ ,<sup>150b</sup>  $150.4^\circ$ ,<sup>1571a</sup>  $150^\circ$ ,<sup>158</sup>, <sup>1788</sup>  $148-9^\circ$ ,<sup>637</sup>  $148^\circ$ ,<sup>1510</sup>, <sup>1892a</sup>  $143^\circ$ ; <sup>454</sup>, <sup>1668</sup>  $d_0$  1.036, 1.071 <sup>637</sup>  $d$  9/0 1.0282,<sup>1041</sup>  $d$  0/4 1.03909,<sup>1782</sup> 1.0290,<sup>1265</sup> 1.0281,<sup>772</sup>  $d$  10.1/4 1.0170,<sup>1041</sup>  $d$  10.1/10.1 1.0173,<sup>1041</sup>  $d_{15}$  1.021,<sup>637</sup>  $d$

- 15/4 1.02356, 1.055,<sup>637</sup> 1.0155,<sup>765</sup> d 17/4 1.0100,<sup>412d</sup> d 18.4/4 1.008,<sup>1468</sup> d<sub>20</sub> 1.015,<sup>454</sup> d 20/4 1.0152,<sup>850</sup> 1.0126,<sup>146</sup> d 24.2/4 1.00572,<sup>1301</sup> d 25/4 1.0140,<sup>39</sup> 1.0125,<sup>1071</sup> d 30/4 1.00811,<sup>1782</sup> d 31.5/4 0.9948,<sup>1265</sup> d 50/4 0.9885,<sup>1071</sup> d 61/4 0.9627,<sup>1265</sup> d 80/4 0.9537,<sup>1071</sup> d 150/4 0.8740,<sup>1571a</sup> d 151/4 0.8739,<sup>1571a, b</sup> n 13/D 1.5335,<sup>39</sup> n 15/D 1.5298,<sup>765</sup> n 17/D 1.5325,<sup>412d</sup> n 18.5/D 1.5304,<sup>39</sup> n 20/D 1.5257,<sup>850</sup> 1.5266,<sup>146</sup> 1.5300,<sup>39</sup> n 24.2/D 1.52212;<sup>1301</sup> critical temperature 359.3°; <sup>1468</sup> heat of formation 41.8 cal; <sup>150b</sup> heat of combustion, at constant pressure 675.36,<sup>1775</sup> (vapors) 675.4 cal, (liquid) 732.6 cal,<sup>150a</sup> at constant volume (liquid) 731.2 cal; dielectric constant (K) 17.3 at 17.6°,<sup>937</sup> 17.2 at 18°;<sup>1207</sup> specific conductivity  $2.48 \times 10^{-5}$ ; <sup>1207</sup> viscosity (g/cm/sec) 0.00673 at 25°, 0.00541 at 50°, 0.00427 at 80°,<sup>1071</sup> 0.00316 at 100°, 0.00263 at 125°;<sup>1072</sup> surface tension at 18.4° 31.53,<sup>1468</sup> 33.52,<sup>1468</sup> at 46° 28.36,<sup>1265</sup> 30.37°;<sup>1265</sup> free surface energy  $E_s$  66.0.<sup>748</sup>
- 1-Methylallyl,  $\text{CH}_2:\text{CHCHMeNCS}$ , b<sub>34</sub> 70–2°; <sup>1017</sup> b. 158–9°; <sup>1829</sup> d 20/4 0.9720.<sup>1285</sup>
- 2-Methylallyl,  $\text{CH}_2:\text{CMeCH}_2\text{NCS}$ , b<sub>5</sub> 56–9°, b<sub>10</sub> 64°,<sup>263</sup> b<sub>12</sub> 60°,<sup>1017</sup> b<sub>20</sub> 69°, 62°, b<sub>25</sub> 78°, b<sub>36</sub> 85°, b<sub>50</sub> 89–90°, b<sub>760</sub> 169–70°, b. 179°; <sup>263</sup> d 20/4 0.9926; n 20/D 1.5220.<sup>1748</sup>
- Crotyl,  $\text{MeCH}:\text{CHCH}_2\text{NCS}$ , b. 179°,<sup>813, 814</sup> 175–6°,<sup>1572</sup> 174°,<sup>1670</sup> 158–9°,<sup>233</sup> b<sub>11</sub> 67–8°,<sup>1017</sup> b<sub>111</sub> 104.5–5.0°; <sup>1623c</sup> d 11/4 0.9933,<sup>1670</sup> d 15/4 0.9941; <sup>1572</sup> n 20/D 1.5240.<sup>1572</sup>
- cis-Crotyl, b<sub>11</sub> 71–3°.<sup>1016</sup>
- 3-Butenyl,  $\text{CH}_2:\text{CHCH}_2\text{CH}_2\text{NCS}$ , b<sub>12</sub> 64°,<sup>1013.8</sup> b. 174° dec; <sup>1670</sup> d 11/4 0.9933.<sup>1670</sup>
- 2-Methyl-2-butenyl,  $\text{MeCH}:\text{CMeCH}_2\text{NCS}$ , b. 190°.<sup>1813, 1814</sup>
- 2-Pentenyl,  $\text{MeCH}_2\text{CH}:\text{CHCH}_2\text{NCS}$ , b. 186–8°.<sup>1285</sup>
- 2-*i*-Pentenyl,  $\text{Me}_2\text{C}:\text{CHCH}_2\text{SCN}$ , b<sub>35</sub> 65–70°; d<sub>20</sub> 0.9468; n 20/D 1.491.<sup>1728</sup>
- 4-Pentenyl,  $\text{CH}_2:\text{CHCH}_2\text{CH}_2\text{CH}_2\text{NCS}$ , b<sub>12</sub> 75°; n 25/D 1.5118.<sup>1013.8</sup>
- 1-Ethylallyl,  $\text{CH}_2:\text{CHCHEtNCS}$ , b<sub>18</sub> 71°, b. 176–8°; d 20/4 0.9510.<sup>1285</sup>
- 3-Ethylallyl,  $\text{EtCH}:\text{CHCH}_2\text{SCN}$ , b<sub>1.6</sub> 55°; d 20/4 0.9608.<sup>1285</sup>
- 1-Ethyl-2-methylallyl,  $\text{CH}_2:\text{CMeCHEtNCS}$ , b<sub>10</sub> 75–90°, b<sub>760</sub> 190–200°.<sup>263</sup>
- 1-Ethyl-2-propylallyl, b<sub>10</sub> 105–10°.<sup>230</sup>

Oleyl,  $C_{17}H_{33}CH_2NCS$ ,  $b_{0.4}$  200–10°;  $n$  18.5/D 1.6866.<sup>1843</sup>  
 2,3-Butadienyl,  $CH_2:C:CHCH_2NCS$ ,  $b_{14}$  65–75°;  $d$  20/4  
 1.0403.<sup>301</sup>

#### SUBSTITUTED ALKYL ISOTHIOCYANATES

$FCH_2(CH_2)_3CH_2NCS$ ,  $b_9$  104.5–5°;  $n$  15/D 1.4917.<sup>1343</sup>  
 $FCH_2(CH_2)_4CH_2NCS$ ,  $b_8$  116–16.5;  $n$  25/D 1.4882.<sup>1343</sup>  
 $ClCH_2CH_2NCS$ ,  $b_{13}$  80°;  $d$  20/4 1.265.<sup>241</sup>  
 $CH_2:CClCH_2NCS$ , f.p. –100°;  $b_{760}$  151.9 ± 0.1°, <sup>1781</sup>  $b_{755}$  151.8–  
 2.2°, <sup>40</sup>  $b$ . 182° cor; <sup>438</sup> 180–1°, <sup>779a</sup>  $d$  12/12 1.27, <sup>779a</sup>  $d$  25/4  
 1.0140;  $n$  13/D 1.5335, <sup>40</sup>  $n$  18.5/D 1.5304,  $n$  20/D 1.5300.<sup>40</sup>  
 $BrCH_2CH_2NCS$ ,  $b_{15}$  102–8°.<sup>387</sup>  
 $BrCH_2CHBrCH_2NCS$ ,  $d$ . 17/4 1.9684.<sup>548</sup>  
 $CH_2:CBrCH_2NCS$ ,  $b_{14}$  98–100°, <sup>228</sup>  $b_{10}$  77.5–9.5°, 100°, <sup>1583</sup>  $b$ .  
 200°. <sup>779b</sup>,  $d$   
 $ClCH_2CH(OH)CH_2NCS$ ,  $b$ . 182°.<sup>438</sup>  
 Glucosyl 1-isothiocyanate,  $[\alpha]$  25/D –12.8° ( $C$  0.7509,  $H_2O$ ).<sup>246.5</sup>  
 Acetoisothiocyanoglucose,  $m$ . 111.5–3.0°.<sup>543b</sup>  
 1-isothiocyano-2,3,4,6-tetraacetyl- $\beta$ -*D*-glucose,  $m$ . 114°.<sup>1816.5</sup>  
 2,3,4,6-Tetra-acetyl- $\beta$ -*D*-glucosaminyl isothiocyanate,  $m$ .  
 16.1°.<sup>1243.4</sup>  
 Heptaacetylactoseisothiocyanate,  $m$ . 170°.<sup>913</sup>  
 $MeOCH_2NCS$ ,  $b_{10}$  33.5–5.5°, <sup>1582</sup>  $b_{30}$  56–60°,  $b_{770}$  138°.<sup>915</sup>  
 $EtOCH_2NCS$ ,  $b_{10}$  46–8°, <sup>1582</sup>  $b_{98}$  93–7°.<sup>915</sup>  
 $PrOCH_2NCS$ ,  $b_{10}$  61.5–2.5°.  
 $Me_2CHOCH_2NCS$ ,  $b_{10}$  52–3°.<sup>1582</sup>  
*i*- $AmOCH_2NCS$ ,  $b_{22}$  111–4°,  $b_{34}$  122–25°,  $b$ . 208–10°.<sup>915</sup>  
*i*- $HexOCH_2NCS$ ,  $b_{10}$  97–8°.<sup>1582</sup>  
*c*- $HexOCH_2NCS$ ,  $b_{10}$  109–10°.<sup>1582</sup>  
 2,4- $Cl_2C_6H_3OCH_2NCS$ ,  $m$ . 38–40°;  $b_{0.1}$  108–10°.<sup>98</sup>  
 $MeOCH_2CH_2NCS$ ,  $b_{23.5}$  88.5–92°;  $n$  24.5/D 1.5010.<sup>219</sup>  
 $(EtO)_2CHCH_2NCS$ ,  $b_2$  63–5°.<sup>369.5</sup>  
 $MeOCH_2CH_2CH(CH:CH_2)NCS$ ,  $b_5$  87–8°; <sup>499.5</sup>  $n$  25/D 1.5020.<sup>498</sup>  
 $BuOCH_2CH_2CH(CH:CH_2)NCS$ ,  $b_5$  118–9°; <sup>499.5</sup>  $n$  25/D  
 1.4880.<sup>498</sup>  
 $MeOCH_2CH_2CH:CHCH_2NCS$ ,  $b_5$  105–7°; <sup>499.5</sup>  $n$  25/D 1.5154.<sup>498</sup>  
 $BuOCH_2CH_2CH:CHCH_2NCS$ ,  $b_5$  136–40°; <sup>499.5</sup>  $n$  25/D 1.4985.<sup>498</sup>  
 $Me_3SiCH_2NCS$ ,  $b_{25}$  90°.<sup>1325</sup>  
 $(EtO)_3SiCH_2NCS$ ,  $b_3$  120°.<sup>1325</sup>

- EtSCH<sub>2</sub>NCS, b<sub>30</sub> 106°. <sup>188.5</sup>  
 MeSCH<sub>2</sub>CH<sub>2</sub>NCS, b<sub>2</sub> 85°; n 25/D 1.5767; <sup>1008</sup> sulfone, m. 47°. <sup>782b</sup>  
 MeSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NCS, b<sub>9</sub> 116°, b<sub>12</sub> 121°; n 25/D 1.5610; <sup>1008</sup>  
 sulfone, m. 48°, <sup>262a</sup> 46–8°; <sup>1928</sup> b<sub>3</sub> 200°. <sup>262a</sup>  
 PhCH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NCS, b<sub>0.2</sub> 102–5°; n 22/D 1.5770. <sup>1738.5</sup>  
 MeSCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>NCS, b<sub>9</sub> 130–40°; <sup>1578</sup> b<sub>12</sub> 136°; <sup>1008</sup> n 25/D  
 1.5518; <sup>1008</sup> sulfoxide, b<sub>0.01</sub> 125–35°; <sup>1578</sup> sulfone, m. 60.5°, 60°.  
 MeSCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>NCS, b<sub>10</sub> 155°; n 25/D 1.5422. <sup>1008</sup>  
 MeSCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>NCS, b<sub>0.5</sub> 119°; n 25/D 1.5336. <sup>1008</sup>  
 MeSCH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>NCS, b<sub>0.3</sub> 117°; n 25/D 1.5274. <sup>1008</sup>  
 MeSCH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>2</sub>NCS, b<sub>0.3</sub> 122°; n 25/D 1.5242. <sup>1008</sup>  
 MeSCH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>NCS, b<sub>0.2</sub> 130°; n 25/D 1.5189. <sup>1008</sup>  
 CH<sub>2</sub>:CHSCH<sub>2</sub>CH<sub>2</sub>NCS, sulfoxide n 25/D 1.5862. <sup>1023</sup>  
 ClCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>NCS, b. 116–8°; sulfoxide, m. 55–8°;  
 sulfone, m. 54°. <sup>1023</sup>  
 MeSOCH:CHCH<sub>2</sub>CH<sub>2</sub>NCS, b<sub>0.015</sub> 125–30°; [α] 19/D  
 –102°. <sup>1578.5</sup>  
 Et<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCS, b<sub>11</sub> 98°; d 20/4 0.9659; n 20/D 1.5059. <sup>1580</sup>  
 Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NCS, b<sub>10</sub> 41–2°, <sup>1585</sup> 91–2°, <sup>522</sup> d 20/4 0.9747; n  
 20/D 1.5072; <sup>1585</sup> picrate m. 109°. <sup>1585</sup>  
 Et<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NCS, b<sub>3.5</sub> 95°; n 25/D 1.4968. <sup>1634</sup>  
 Et<sub>2</sub>NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CHMeNCS, m. 85°; <sup>1580</sup> b<sub>9</sub> 124–6°; <sup>622, 1585</sup> d  
 20/4 0.9289; n 20/D 1.4925. <sup>1585</sup>

## PHENYL ISOTHIOCYANATES

- Phenyl, C<sub>6</sub>H<sub>5</sub>NCS, m. –21° cor; <sup>1590</sup> b<sub>760</sub> 221° cor <sup>1388</sup> 218.5°, <sup>936</sup> b<sub>5</sub>  
 78.5°, <sup>1477b</sup> 80.5°, <sup>936a</sup> b<sub>9</sub> 88–90°, <sup>1585</sup> 89–90°, <sup>522</sup> b<sub>10</sub> 91.8°, <sup>1477b</sup> 91.2°,  
<sup>936a</sup> b<sub>12</sub> 100–1°, <sup>1817</sup> b<sub>14</sub> 89.3°, b<sub>15</sub> 98.86°, <sup>1477b</sup> 99.4°, <sup>936a</sup> 99.9°, <sup>1477b</sup>  
 b<sub>16</sub> 101.3°, <sup>1477a</sup> b<sub>20</sub> 106.2°, <sup>1477b</sup> 110–12°, <sup>1701</sup> b<sub>25</sub> 111.6°, <sup>936a</sup> b<sub>32</sub>  
 117.1°, b<sub>37</sub> 121.0°, <sup>936a, b</sup> b<sub>50</sub> 126.6°, <sup>936a</sup> b<sub>63</sub> 131.8°, <sup>936a, b</sup> b<sub>100</sub>  
 147.7°, <sup>1477b</sup> b<sub>700</sub> 216.8°, <sup>1477b</sup> b<sub>720.4</sub> 219–19.2°, <sup>195</sup> b<sub>748</sub> 220°, <sup>1301</sup> b<sub>749</sub>  
 219.8°, <sup>1571b</sup> b<sub>754</sub> 222°, <sup>1847</sup> b<sub>762</sub> 222°, <sup>814</sup> b. 222°, <sup>412d</sup> 221.5°, <sup>150b</sup>  
 221°, <sup>1847</sup> 220.41°, <sup>1477a, b</sup> 218.5°, <sup>936a</sup> 218°, <sup>1207</sup> d 0/4 1.1503, <sup>1847</sup>  
 d 4/4 1.1477, <sup>1388</sup> d<sub>13.2</sub> 1.1400, <sup>13.2</sup> d 15/4 1.135, <sup>412d</sup> d 15/15  
 1.1382, <sup>1388</sup> d 23.4/4 1.1289, <sup>412d, 1301</sup> d 25/4 1.1288, <sup>1071</sup> 1.1278, <sup>1847</sup>  
 d 25/25 1.1314, <sup>1388</sup> d 30/4 1.1234, <sup>1265</sup> d 35/4 1.1207, <sup>1071</sup> 1.1202, <sup>1071</sup>  
 d<sub>38.8</sub> 1.1148, <sup>195</sup> d 40/4 1.1137, <sup>1265</sup> d 42.5/4 1.1247, <sup>412d</sup> d 50/4  
 1.1044, <sup>1265</sup> 1.1061, <sup>1071</sup> d<sub>54.8</sub> 1.1000, <sup>195</sup> d<sub>78.6</sub> 1.0781, d<sub>109.2</sub> 1.0493,  
 d<sub>152.2</sub> 1.0083, <sup>195</sup> d 220/4 0.9398; <sup>1571</sup> n 20/D 1.6508, <sup>1585</sup> n 23.4/D

- 1.64918,<sup>1128, 1301</sup>  $n_{23.5/D}$  1.6465; <sup>1701</sup> heat of formation —46.5 cal; <sup>150b</sup> molecular heat of combustion 1019.0 cal at constant volume, 1020.3 cal at constant pressure; <sup>150a</sup> dipole moment 2.76; <sup>144</sup> association at b.p. 0.99; <sup>1847</sup> dielectric constant 8.5, <sup>835</sup> at 20° 10.0, <sup>1207</sup> 11°; <sup>1847</sup> specific conductivity  $1.4 \times 10^{-6}$ , <sup>1207</sup>  $2.55 \times 10^{-5}$ , <sup>1207</sup>  $0.18 \times 10^{-6}$ ; <sup>1207</sup> surface tension at 13.2° (dyn/cm) 41.51, <sup>195</sup> at 38.8° 38.40, <sup>1265</sup> 38.47, at 54.8° 36.58, at 109.2° 30.74, at 152.2° 26.35; <sup>195</sup> viscosity (g/cm/sec) 0.01397 at 25°, <sup>1071</sup> 0.01199 at 35°, 0.00978 at 50°; <sup>1071</sup> parachor 305.4.<sup>1391</sup>
- PhNCS<sup>35</sup>,  $b_{28}$  118°.<sup>1879</sup>
- p*-FC<sub>6</sub>H<sub>4</sub>NCS, b. 228°.<sup>474</sup>
- ClC<sub>6</sub>H<sub>4</sub>NCS, *o*-, b. 248°, <sup>699</sup>  $b_{1.5}$  91°;  $n_{23.5/D}$  1.6604; <sup>1701</sup> *m*-, b. 249–50°; <sup>813, 814</sup> *p*-, m. 47°, <sup>132</sup> 45°, <sup>329</sup> 44.5°, <sup>813, 814</sup> 40°; <sup>1147</sup> b. 249–50°.<sup>813, 814</sup>
- BrC<sub>6</sub>H<sub>4</sub>NCS, *o*-,  $b_{770}$  257°; <sup>471</sup> *m*-, b. 256°; <sup>624a</sup> *p*-, m. 61°, <sup>1863</sup> 59°.<sup>1817</sup>
- IC<sub>6</sub>H<sub>4</sub>NCS, *o*-, m. 39°; *m*-, m. 46°; <sup>471</sup> *p*-, m. 65°.<sup>1147</sup>
- O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NCS, *o*-, m. 76°, <sup>493</sup> 74°, <sup>48</sup> 72°; <sup>505</sup> *m*-, m. 60°; <sup>1546</sup> *p*-, m. 113°.<sup>892</sup>
- Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCS, 2,3-, b. 256–8°; <sup>471</sup> 2,4-, m. 40°, 39°;  $b_{17.5}$  208°; <sup>329</sup> 3,4-,  $b_{2.0}$  134.8–5.9°.<sup>120</sup>
- 2,4-Br<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCS, m. 63°, <sup>330</sup> 59.5°.<sup>329</sup>
- Hydroxyphenyl, HOC<sub>6</sub>H<sub>4</sub>NCS, *m*-, m. 62°; <sup>818</sup>  $b_{0.3}$  120–4°; <sup>521.5</sup> *p*-, m. 43°; <sup>1673</sup>  $b_{0.3}$  119–22°; <sup>521.5</sup>  $b_{11}$  175–85°.<sup>1673</sup>
- MeOC<sub>6</sub>H<sub>4</sub>NCS, *o*-, m. 194°; <sup>624a</sup>  $b_{760}$  267°; <sup>471</sup> *m*-,  $b_{0.45}$  105–6°; <sup>512.5</sup>  $b_{760}$  267°; <sup>471</sup>  $d_{30/4}$  1.45; <sup>512.5</sup>  $n_{28.4/D}$  1.5867; <sup>512.5</sup> *p*-, m. 148°; <sup>624a</sup> b. 270°.<sup>1549a</sup>
- EtOC<sub>6</sub>H<sub>4</sub>NCS, *o*-, b. 223–5°; <sup>471</sup> *m*-,  $b_{758}$  278°; <sup>471</sup> *p*-, m. 76°, <sup>470</sup> 62.5°; <sup>624a</sup> 61°.<sup>1817</sup>
- PrOC<sub>6</sub>H<sub>4</sub>NCS, *m*-,  $b_{0.01}$  105–7°; <sup>817.5</sup> *p*-,  $b_{15}$  163–8°.<sup>847</sup>
- p*-Me<sub>2</sub>CHOC<sub>6</sub>H<sub>4</sub>NCS,  $b_{28}$  170–2°.<sup>446</sup>
- BuOC<sub>6</sub>H<sub>4</sub>NCS, *m*-,  $b_{0.02}$  120–2°; <sup>818</sup> *p*-,  $b_{15}$  179–81°; <sup>847</sup>  $b_{25.5}$  191.5–93°; <sup>447</sup>  $b_{0.25}$  110–7°; <sup>1284</sup>  $n_{23/D}$  1.5596.<sup>1284</sup>
- p*-Me<sub>2</sub>CHCH<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>NCS,  $b_{15}$  172°; <sup>847</sup>  $b_{35}$  193–4°.<sup>447</sup>
- p*-AmOC<sub>6</sub>H<sub>4</sub>NCS,  $b_{0.8}$  147–50°; <sup>1284</sup>  $b_{25}$  203–5°; <sup>446</sup>  $n_{23/D}$  1.5901.<sup>1284</sup>
- p*-Me<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>NCS,  $b_{15}$  188–90°.<sup>847</sup>
- Allyloxyphenyl, *o*-,  $b_{0.8}$  110–8°; <sup>1284</sup>  $n_{23/D}$  1.6242; <sup>1284</sup> *m*-,  $b_{0.03}$  110–12°.<sup>819</sup>

$m$ -CH<sub>2</sub>:CMeCH<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>NCS,  $b_{0.03}$  125–7°.<sup>819</sup>  
 2-Pyridyloxyphenyl,  $p$ -,  $b$ . 50–1°.<sup>446</sup>  
 PhOC<sub>6</sub>H<sub>4</sub>NCS,  $m$ . 42°.<sup>390</sup>  
 2,5-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCS,  $m$ . 33°.<sup>957</sup> 32°; <sup>471</sup>  $b_{16}$  178–80°.<sup>957</sup>  
 3,4,5-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>3</sub>NCS,  $m$ . 65°.<sup>253</sup>  
 $p$ -AcHNC<sub>6</sub>H<sub>4</sub>NCS,  $m$ . 193°.<sup>1817</sup>  
 $p$ -Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NCS,  $m$ . 69–71°.<sup>446</sup>  
 $p$ -Et<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NCS,  $b_{1.2}$  148°;  $n$  25/D 1.6690.<sup>1176</sup>  
 2-Pyridylphenyl, C<sub>5</sub>H<sub>4</sub>NC<sub>6</sub>H<sub>4</sub>NCS,  $p$ -,  $m$ . 50–2°.<sup>446</sup> 51°.<sup>447</sup>  
 $p$ -MeSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NCS,  $m$ . 137°.<sup>446</sup>  
 $p$ -EtSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NCS,  $m$ . 118°.<sup>1711</sup>  
 $p$ -NCC<sub>6</sub>H<sub>4</sub>NCS,  $m$ . 45°.<sup>471</sup> 122°.<sup>530</sup>  
 $p$ -MeCOC<sub>6</sub>H<sub>4</sub>NCS,  $b_{6.2}$  112°;  $n$  25/D 1.6453.<sup>1176</sup>  
 $p$ -EtCOC<sub>6</sub>H<sub>4</sub>NCS,  $m$ . 65°.<sup>446</sup>  
 $p$ -PrCOC<sub>6</sub>H<sub>4</sub>NCS,  $m$ . 37°.<sup>446</sup>  
 $p$ -H<sub>2</sub>NSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NCS,  $m$ . 212–4°.<sup>1172</sup>  
 $m$ -OCNC<sub>6</sub>H<sub>4</sub>NCS,  $m$ . 4–6°;  $b_{14}$  140–2°.<sup>1660</sup>

## BENZYL ISOTHIOCYANATES

Benzyl, PhCH<sub>2</sub>NCS,  $b_{1.3}$  90–1°.<sup>512.4</sup>  $b_3$  105–7°.<sup>987</sup>  $b_{11}$  125°.<sup>1595</sup>  
 123.4°.<sup>1580</sup>  $b_{12}$  124–5°.<sup>1595</sup>  $b_{17}$  140–1°.<sup>130</sup>  $b$ . 221°.<sup>1388</sup> 243°; <sup>813</sup>  
<sup>814</sup>  $d$  15/4 1.1246;<sup>765</sup>  $d$  20/4 1.1234;<sup>765</sup>  $n$  20/D 1.6039;<sup>1580</sup>  
 1.5955.<sup>512.4</sup>  
 ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NCS,  $o$ -,  $b_6$  138°;  $m$ -,  $b_6$  140–5°;  $p$ -,  $b_4$  130–3°.<sup>1796</sup>  
 BrC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NCS,  $o$ -,  $b_5$  130–4°;  $m$ -,  $b_5$  147°;  $p$ -,  $b_{5-7}$  140–4°.<sup>1796</sup>  
 IC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NCS,  $m$ -,  $b_{3-4}$  162°;  $p$ -,  $b_{3-4}$  167°.<sup>1796</sup>  
 MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NCS,  $o$ -,  $m$ . 28°;  $b_4$  133°; <sup>1013.7</sup>  $p$ -,  $b_{0.7}$  133°.<sup>1012.5</sup>  
 $b_{16}$  170–5°; <sup>223</sup>  $n$  25/D 1.5935.<sup>1012.5</sup>  
 $p$ -AcNHC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NCS,  $m$ . 164°.<sup>1327</sup>

## TOLYL AND XYLIL ISOTHIOCYANATES

Tollyl, MeC<sub>6</sub>H<sub>4</sub>NCS,  $o$ -,  $b$ . 239°.<sup>456, 473</sup> 238–40°.<sup>85</sup> 237°.<sup>1183</sup>  $m$ -,  
 liq at –20°;  $b_{732}$  244°.<sup>473</sup>  $b$ . 244°; <sup>1863</sup>  $p$ -,  $m$ . 26°; <sup>473, 773, 1183</sup>  
<sup>1865</sup>  $b$ . 91°.<sup>1865</sup> 237–9°.<sup>1183</sup>  
 3,4-Cl(Me)C<sub>6</sub>H<sub>3</sub>NCS,  $b_8$  127°.<sup>1865</sup>  
 HO(Me)C<sub>6</sub>H<sub>3</sub>NCS, 3,2-,  $b_{0.3}$  122–6°.<sup>521.5</sup>  
 Xylil, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCS, 1,2,3-,  $b_{760}$  262–3°; <sup>471</sup> 1,3,2-,  $b_{760}$  247°; <sup>471</sup>  
 1,3,4-  $m$ . 31.5°.<sup>1867</sup> 29°.<sup>473</sup> 24°; <sup>1189</sup>  $b$ . 266°; <sup>473</sup> 1,4,2-,  $b$ . 262°.<sup>473</sup>

## OTHER ARYL ISOTHIOCYANATES

- PhCHMeNCS,  $b_{20}$  133–4°, <sup>1156</sup>  $b_{23}$  135–7°; <sup>1156</sup>  $d$  25/25 1.0754, <sup>1156</sup> 1.0719; <sup>1156</sup>  $n$  25/D 1.5780, <sup>1156</sup> *DL*,  $b_{12}$  122–3°;  $n$  25/D 1.5801; <sup>1006</sup> ( $\pm$ )  $b_{12}$  122–3°;  $n$  25/D 1.5801; <sup>1006</sup> (+)  $b_{16}$  126°;  $n$  25/D 1.5802; [ $\alpha$ ] 24/D 17.5 (C 9.8 CHCl<sub>3</sub>; <sup>1066</sup> (–)  $b_{10}$  121°;  $n$  25/D 1.5801; [ $\alpha$ ] 24/D –17.3 (C<sub>10.0</sub> CHCl<sub>3</sub>).<sup>1006</sup>
- PhCH<sub>2</sub>CH<sub>2</sub>NCS,  $m$ . 108°; <sup>116</sup>  $b_{11}$  141–5°, <sup>223</sup> 139–40°;  $d$  20/4 1.0942;  $n$  20/D 1.5904.<sup>1580</sup>
- PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NCS,  $b_{12}$  156–60°. <sup>223</sup>
- PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NCS,  $b_{12}$  166–74°. <sup>223</sup>
- EtC<sub>6</sub>H<sub>4</sub>NCS, *o*-,  $b$ . 240–5° dec; <sup>1382</sup> *p*-,  $b$ . 255.5–256°. <sup>1183</sup>
- p*-PrC<sub>6</sub>H<sub>4</sub>NCS,  $b$ . 263°, <sup>562</sup>  $b_{20}$  144–54°. <sup>847</sup>
- p*-Me<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>NCS,  $b_{15}$  140–5°. <sup>847</sup>
- p*-BuC<sub>6</sub>H<sub>4</sub>NCS,  $b_{14}$  150–4°, <sup>847</sup> 154–7°;  $n$  23/D 1.5942. <sup>1284</sup>
- p*-Me<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>NCS,  $m$ . 42°;  $b$ . 277°. <sup>1359</sup>
- p*-Me<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NCS,  $b_{15}$  189–90°. <sup>847</sup>
- p*-Me<sub>2</sub>EtCC<sub>6</sub>H<sub>4</sub>NCS,  $b_{0.2}$  104°. <sup>1176</sup>
- 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>NCS,  $m$ . 64°. <sup>491</sup>
- 2,3,4,6-Me<sub>4</sub>C<sub>6</sub>HNCS,  $m$ . 65°. <sup>815</sup>
- Me<sub>5</sub>C<sub>6</sub>NCS,  $m$ . 86°. <sup>473</sup>
- 2,4-Me(*t*-Bu)C<sub>6</sub>H<sub>3</sub>NCS,  $m$ . 46°;  $b$ . 275–80° dec. <sup>488</sup>
- 2,6,4-Me<sub>2</sub>(*t*-Bu)C<sub>6</sub>H<sub>2</sub>NCS,  $m$ . 83°. <sup>115</sup>
- p*-Me<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>NCS,  $b$ . 245–70° dec. <sup>1458</sup>
- Ph<sub>2</sub>CHNCS,  $m$ . 61°, <sup>1874</sup> 60°, <sup>402</sup> 58°; <sup>223</sup>  $b_{37-38}$  222–25°. <sup>1874</sup>
- o*-ClC<sub>6</sub>H<sub>4</sub>CHPhNCS,  $b_{1.5}$  186–9°. <sup>1899.5</sup>
- Me<sub>2</sub>PhCNCS,  $b_{0.7}$  83°,  $b_{23}$  82–6°;  $d$  25/25 1.0537, 1.0565;  $n$  25/D 1.5670, 1.5678. <sup>1156</sup>
- Ph<sub>3</sub>CNCS,  $m$ . 137°. <sup>235</sup>
- PhC<sub>6</sub>H<sub>4</sub>NCS, *o*-,  $b_{0.04}$  122°;  $n$  25/D 1.6572, <sup>1176</sup> *p*-,  $m$ . 70°, <sup>352</sup> 64.5°, <sup>1701</sup> 60°, <sup>238</sup> 53°. <sup>515</sup>
- C<sub>10</sub>H<sub>7</sub>NCS,  $\alpha$   $m$ . 59°, <sup>471</sup> 58.5°, <sup>1701</sup> 58°, <sup>1230</sup> 57°, <sup>472</sup>  $\beta$   $m$ . 63°, <sup>374</sup> 62°. <sup>1701</sup>
- $\alpha$ -C<sub>10</sub>H<sub>7</sub>CH<sub>2</sub>NCS,  $b_{2-3}$  165–70°. <sup>928</sup>
- ( $\alpha$ -C<sub>10</sub>H<sub>7</sub>)<sub>2</sub>CHNCS,  $m$ . 125°. <sup>1876</sup>
- 2-*p*-CymylNCS, C<sub>10</sub>H<sub>13</sub>NCS,  $b_3$  118–22°,  $b$ . 267–8°;  $n$  20/D 1.5973. <sup>1701</sup>
- 5-Acenaphthenyl, C<sub>12</sub>H<sub>8</sub>NCS,  $m$ . 96°. <sup>1457</sup>
- 2-Fluorenyl, C<sub>13</sub>H<sub>9</sub>NCS,  $m$ . 107°. <sup>1060.5</sup>



Anthranyl,  $C_{14}H_9NCS$ ,  $\alpha$ -, m.  $99^\circ$ ;  $\beta$ -, m.  $196^\circ$ .<sup>107</sup>  
 9-Phenanthryl,  $C_{14}H_9NCS$ , m.  $103^\circ$ ,<sup>1701</sup> 99.5–101.5.<sup>1213</sup>  
 1-Pyrenyl,  $C_{18}H_9NCS$ , m.  $125.5^\circ$ .<sup>1701</sup>  
 Chrysyl,  $C_{18}H_{11}NCS$ , m.  $176^\circ$ .<sup>2</sup>  
 2-Isothiocyano-isocamphene, m.  $84-6^\circ$ .<sup>1157</sup>

## HETEROCYCLIC ISOTHIOCYANATES

Tetrahydrofurfuryl,  $C_4H_7O \cdot CH_2NCS$ ,  $b_{18}$  122– $2.5^\circ$ ,<sup>1641</sup> 122– $5^\circ$ ; <sup>1075.6</sup> d 19.5/4 1.1710; n 20/D 1.5055.<sup>1075.6</sup>  
 2- $C_4H_7O \cdot (CH_2)_3NCS$ ,  $b_{28}$  155– $8^\circ$ ; d 20.5/4 1.0929; n 21.5/D 1.4982.<sup>1075.6</sup>  
 2- $C_4H_8O \cdot CH(SCN)CH_2NCS$ , m.  $77^\circ$ ,<sup>1640</sup>  $75^\circ$ .<sup>1075.7</sup>  
 (Isothiocyanomethyl)tetrahydropyran,  $C_5H_9O \cdot CH_2NCS$ , 2-,  $b_6$  110– $12^\circ$ ; d 21/4 1.1303; n 21/D 1.550; <sup>1075.6</sup> 3-,  $b_3$  108– $9^\circ$ ; d 21.5/4 1.144; n 22/D 1.5097.<sup>1075.6</sup>  
 Thenyl,  $C_4H_3S \cdot CH_2NCS$ ,  $b_{20}$  141– $2^\circ$ .<sup>225</sup>  
 Pyridyl,  $C_5H_4N \cdot CH_2NCS$ , 2-, m.  $111^\circ$ ; <sup>517</sup> 3-,  $b_{14}$   $104^\circ$ .<sup>1027.5</sup>  
 6-Isothiocyanoquinoline, m.  $94^\circ$ ; <sup>712</sup> MeI m.  $238^\circ$ .<sup>517</sup>  
 4-Amino-6-isothiocyanoquinoline, (dec) 270– $5^\circ$ .<sup>1266.5</sup>

## ISOTHIOCYANO-ACIDS

Isothiocyanoacetic,  $CH_2(NSC)COOH$ , Ethyl ester,  $b_7$  104– $6^\circ$ ,<sup>923</sup>  $b_{10}$   $110^\circ$ ,<sup>916</sup>  $b_{12}$  112– $3^\circ$ ,<sup>916</sup>  $110^\circ$ ,<sup>1019</sup>  $b_{15}$   $113^\circ$ ,<sup>916</sup> b.  $215^\circ$ ,<sup>916</sup>  $225^\circ$ ; <sup>916</sup> d 18/4 1.1649,<sup>1019</sup> d 20/4 1.1710; n 20/D 1.5038;<sup>916</sup>  $CH_2(NCS)CONHCOOR$ , Et, m.  $170^\circ$ ; *i*-Am, m.  $147^\circ$ .<sup>570</sup>  
 Isothiocyanopropionic,  $CH_2(NCS)CH_2COOH$ , esters: Me,  $b_1$  110– $2^\circ$ ; d 20/4 1.193; n 25/D 1.5036;<sup>623.5</sup> Et, n 25/D 1.4904.<sup>623.5</sup>  
 $\alpha$ -Isothiocyanopropionic,  $MeCH(NCS)COOH$ , Ethyl ester, *DL*  $b_{13}$  93.5– $4.5^\circ$ ; d 20/4 1.0985; n 20/D 1.4915; *D*  $b_{12}$  100– $1^\circ$ ,<sup>925</sup>  $b_{16}$  106– $8^\circ$ ; <sup>925</sup> n 20/D 1.4935;<sup>925</sup>  $[\alpha]$  20/D  $32.07^\circ$ ,<sup>925</sup>  $29.77^\circ$ .<sup>925</sup>  
 Isothiocyanobutyric,  $CH_2(NCS)CH_2CH_2COOH$ , Methyl ester,  $b_{0.17}$  64– $7^\circ$ ,<sup>623.5</sup>  $b_{0.2}$   $70^\circ$ ; <sup>1011</sup> d 20/4 1.135; n 25/D 1.5059,<sup>623.5</sup> 1.5066.<sup>1011</sup>  
 Isothiocyanocaproic,  $CH_2(NCS)CH_2(CH_2)_3COOH$ ,  $b_{0.30}$  120– $2^\circ$ ; d 20/4 1.101; n 25/D 1.5000.<sup>623.5</sup>  
 $\alpha$ -Isothiocyano-*i*-caproic,  $Me_2CHCH_2CH(NCS)COOH$ ,  $b_{0.2}$   $79^\circ$ .<sup>1031</sup>

Isothiocyanocapric,  $\text{CH}_2(\text{NCS})\text{CH}_2(\text{CH}_2)_7\text{COOH}$ , Methyl ester,  $b_{0.1}$  166–8°;  $d$  20/4 1.022;  $n$  25/D 1.4879.<sup>623.5</sup>

Isothiocyanobenzoic,  $\text{HOOC}\text{C}_6\text{H}_4\text{NCS}$ , *m*-,  $m$ . 165°,<sup>1660</sup> 163°;<sup>253</sup> *p*-,  $m$ . 220°; Esters: Et,  $b$ . 296°;<sup>253</sup> Pr,  $m$ . 72°.<sup>253</sup>

Isothiocyanosalicylic, 3,4-(HO)(HOOC) $\text{C}_6\text{H}_3\text{NCS}$ ,  $m$ . 195–7°;<sup>521</sup> Esters: Me,  $m$ . 75°,<sup>67</sup> 74°;<sup>521</sup> Et,  $m$ . 47°;<sup>67</sup> Phenyl,  $m$ . 93°.<sup>67</sup>

*p*-Isothiocyanomethylbenzoic, *p*- $\text{HOOC}\text{C}_6\text{H}_4\text{CH}_2\text{NCS}$ , Methyl ester,  $b_{0.3}$  138–9°;  $d$  25/25 1.219;  $n$  25/D 1.5822.<sup>499</sup>

#### ACYL ISOTHIOCYANATES

Isothiocyanoformic acid,  $\text{HOOCNCS}$ ,  $m$ . 44°,<sup>416a</sup> 43°;<sup>779e</sup> Esters: Me,  $\text{MeOCONCS}$ ,  $b_{12}$  30°;  $d$  15/4 1.152;  $n$  15/D 1.48862;<sup>441a</sup> Et,  $m$ . 43°,<sup>416a</sup> 41°;<sup>779e</sup>  $b_{14}$  43°,<sup>441a</sup>  $b_{21}$  66–7°,<sup>443a</sup>  $b_{30}$  83°,<sup>441a</sup>  $b$ . 180°;<sup>416a, 1443a</sup>  $d$  15/4 1.112;  $n$  25/D 1.47985.<sup>441a</sup>

Acetyl,  $\text{MeCONCS}$ ,  $b_{9-10}$  30–32°,<sup>1244a, b</sup>  $b_{23}$  42.2–3.0°,<sup>765</sup>  $b$ . 134.5°,<sup>440</sup> 132–3°;<sup>1244</sup>  $d$  13.25/4 1.1523,<sup>765</sup>  $d_{16}$  1.151,<sup>1244</sup>  $d$  40/4 1.1230,  $d$  61/4 1.0953,  $d$  75/4 1.0790;  $n$  18.4/D 1.5231,  $n$  31.8/D 1.5144,  $n$  33.5/D 1.5142,  $n$  47/D 1.5056,  $n$  61/D 1.4969,  $n$  69/D 1.4920,  $n$  71/D 1.4917.<sup>765</sup>

*i*-Butyryl,  $\text{Me}_2\text{CHCONCS}$ ,  $b$ . 180°,  $b$ . 159–61°;  $n$  20/D 1.5075.<sup>1244a, b</sup>

Valeryl,  $\text{C}_5\text{H}_{11}\text{CONCS}$ ,  $b_{23}$  108°,  $b_1$  66–70°;  $d$  15/5 1.0165;  $n$  20/D 1.5040.<sup>438</sup>

Palmitoyl,  $b_{10}$  200–5°.<sup>438</sup>

Acrylyl,  $b_{25}$  56–8°.<sup>520.5</sup>

Methacrylyl,  $b_{18}$  60°.<sup>520.5</sup>

Crotonyl,  $b_{17}$  78–80°.<sup>520.5</sup>

$\text{HOCH}_2\text{CONCS}$ ,  $m$ . 106°.<sup>357</sup>

$\text{CH}_3\text{CH}(\text{OH})\text{CONCS}$ ,  $m$ . 90°.<sup>357</sup>

$\text{PhCONCS}$ ,  $b_{15}$  128–31°.<sup>453</sup>

*p*- $\text{BrC}_6\text{H}_4\text{CONCS}$ ,  $m$ . 55°.<sup>62</sup>

*p*- $\text{O}_2\text{NC}_6\text{H}_4\text{CONCS}$ ,  $m$ . 90–2°;  $b_{10}$  187–8°.<sup>1287</sup>

*p*- $\text{Me}_2\text{NC}_6\text{H}_4\text{CONCS}$ ,  $m$ . 58–65°.<sup>1287</sup>

$\text{EtOCSNHCONCS}$ ,  $m$ . 141–42° *cor*.<sup>438</sup>

#### BIS AND TRIS-ISOTHIOCYANATES

$(\cdot\text{CH}_2\text{NCS})_2$ ,  $b_{15}$  151.5–2.0°,  $b_{10}$  144°;  $d$  20/4 1.2646;  $n$  20/D 1.6271.<sup>1917</sup>

$\text{CH}_2(\text{CH}_2\text{NCS})_2$ ,  $b_{10}$  147°.<sup>881</sup>

$(\cdot\text{CH}_2\text{CH}_2\text{NCS})_2$ , oil;  $b_{11}$   $170^\circ$ ,<sup>1023.5</sup>  $b$ .  $147^\circ$ ;  $d$  21.5/4 1.2107;<sup>1657</sup>  
 $n$  19.5/D 1.542.<sup>1657</sup>  
 $\text{CH}_2(\text{CH}_2\text{CH}_2\text{NCS})_2$ ,  $b_3$   $159^\circ$ .<sup>881</sup>  
 $(\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{NCS})_2$ ,  $b_6$   $183-4^\circ$ .<sup>1023.5</sup>  
 $(\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NSC})_2$ ,  $b_{0.4}$   $158-9^\circ$ .<sup>1023.5</sup>  
 $(\cdot\text{CH}_2(\text{CH}_2)_3\text{CH}_2\text{NCS})_2$ ,  $b_{0.4}$   $169.5-71^\circ$ .<sup>1023.5</sup>  
 $\text{O}(\text{CH}_2\text{NCS})_2$ ,  $m$ .  $18.5^\circ$ ; <sup>783</sup>  $b_{2.5-3}$   $94-5^\circ$ ;  $d$  20/4 1.1535;  $n$  20/D  
 1.5520.<sup>783</sup>  
 $\text{O}(\text{CH}(\text{SCN})\text{Me})$ ,  $m$ .  $-7^\circ$ ; <sup>783</sup>  $b_{2-3}$   $94-5^\circ$ ;  $d$  20/4 1.1535;  $n$  20/D  
 1.5520.<sup>783</sup>  
 $\text{C}_6\text{H}_4(\text{NCS})_2$ ,  $o$ -,  $m$ .  $59^\circ$ ; <sup>159</sup>  $m$ -,  $m$ .  $54.8-5.2^\circ$ ,<sup>1900</sup>  $53^\circ$ ; <sup>159</sup>  $p$ -,  $m$ .  
 $131^\circ$ ,<sup>1817</sup>  $130^\circ$ .<sup>1306</sup>  
 2,4-Toluenedi-isothiocyanate,  $m$ .  $54.4^\circ$ ;  $b_4$   $151^\circ$ ,  $b_6$   $168^\circ$ .<sup>1900</sup>  
 $(\cdot\text{C}_6\text{H}_4\text{NCS}-p)_2$ ,  $m$ .  $204^\circ$ ,<sup>1936</sup>  $203^\circ$ .<sup>315</sup>  
 1,4-Di-isothiocyananthroquinone,  $m$ .  $344^\circ$ .<sup>1367</sup>  
 $s$ -Tri-isothiocyanobenzene,  $\text{C}_6\text{H}_3(\text{NCS})_3$ ,  $m$ .  $143^\circ$ .<sup>1176</sup>

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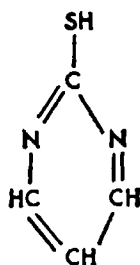
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# Thiopyrimidines and Derivatives

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**2-Thiopyrimidine**

The pyrimidine ring, containing two nitrogen and four carbon atoms, is the nucleus of a host of derivatives, many of which have valuable properties. The most interesting pyrimidine derivatives are those in which hydroxyl and sulfhydryl groups are in positions 2, 4, and 6. 2-Thiopyrimidine and its derivatives are taken up in this chapter. The barbiturates have three hydroxyls in positions 2,4, and 6, and thiobarbiturates have SH in 2 and OH in 4 and 6. All of these exist in tautomeric form.

### **Mercaptopyrimidines**

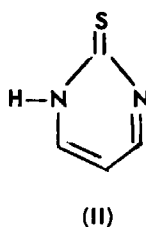
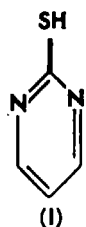
#### **PREPARATION**

Mercaptopyrimidines can be prepared by the reaction of chloropyrimidines with potassium hydrosulfide; <sup>118, 227B, 267, 628, 639, 640</sup>

thus, 4,6-dimethyl-2-chloropyrimidine gives 4,6-dimethyl-2-thiopyrimidine.<sup>628</sup> The isomeric 6-mercaptopyrimidines are obtained similarly from the 6-chloropyrimidines.<sup>110d, 119, 321b, 479, 639, 741a, 741b</sup> Sodium may be added to a solution of the pyrimidine saturated with hydrogen sulfide.<sup>128</sup> 2,6-Dimercaptopyrimidine has been prepared from 2,6-dichloropyrimidine and aqueous potassium hydrosulfide.<sup>740c</sup> It is possible to substitute just one of the chloro groups of a dichloropyrimidine.<sup>478</sup> What appears to be the trimercaptopyrimidine has been obtained from 2,4,5-trichloropyrimidine.<sup>118</sup>

Mercaptopyrimidines, some of which are listed in the table of properties, are also prepared by the condensation of thiourea with: cyanoacetic ester,<sup>703</sup> ethyl cyanoacetate,<sup>366a, 366b</sup> reagents of the type  $\text{NCCHRCOR'}$ ,<sup>712</sup>  $\text{PhCH}_2\text{OCH(CHO)CO}_2\text{Et}$ ,<sup>138</sup> diethyl formylsuccinate,<sup>358b</sup> sodium formyl acetate,<sup>669</sup> ethyl ethyl-acetoacetate,<sup>361</sup>  $\text{EtOCH}_2\text{COCH(OEt)CO}_2\text{Et}$ ,<sup>362, 363a, 363b</sup>  $\text{CF}_3\text{-COCH(CO}_2\text{Et)N:NPh}$ ,<sup>276.5</sup>  $\text{AcCHPrCO}_2\text{Et}$ ,<sup>147a</sup>  $\text{ClCH:C(Et)-CHO}$ ,<sup>624</sup>  $\text{MeC(OMe)}_2\text{CH}_2\text{CH(OMe)}_2$ ,<sup>257</sup>  $\text{PhCH(COCH}_3)_2$ ,<sup>310</sup>  $p\text{-ClC}_6\text{H}_4\text{C(OMe):C(Me)CN}$ .<sup>54</sup> Ammonium thiocyanate has been used instead of thiourea with mesityl oxide.<sup>140</sup>

2-Mercaptopyrimidine is a substituted thiourea and as such it can have either of two structures. According to one, (I), it is a 2-mercaptopyrimidine; according to the other, (II), it is dihydropyrimidine-2-thione:



As each derivative may have at least two structures and correspondingly two, or sometimes more, different systematic names, their nomenclature is very confusing.

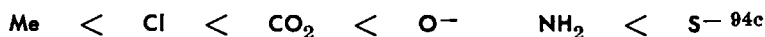
Measurements of ultraviolet absorption spectra indicate that in neutral solution the thione form (II) predominates, and that there is a shift to the mercapto-(I) in alkaline solution.<sup>94c</sup> The absorption in alkaline solution is similar to that of the alkyl-mercaptopyrimidines which must be derivatives of form I.<sup>94c</sup>



The infrared spectra agree with this.<sup>657</sup> In other studies of ultraviolet absorption of substituted thiopyrimidines, the influence of symmetry has been determined.<sup>29c, 680</sup> The ultraviolet absorption maxima for 2-OH-, 2-NH-, and 2-SH-pyrimidines are at 250, 260, and 283 mμ respectively.<sup>29b, 621</sup> The shifts in the ultraviolet wave length for substituents in the 2-position of pyrimidines are in the following order:



but in the 4-position they are:



With methylmercaptopyrimidine,  $\lambda$  decreases in going from pH 1 to 7, and then remains constant.<sup>29b</sup> The close connection between the change in ultraviolet absorption with varying pH shows that absorption is connected with ionization and subsequent ionic rearrangement.<sup>681</sup>

The dipole moment of the 2-mercapto-5-chloropyrimidine is close to zero, showing that the  $\text{CN}_2\text{S}$  group, m.w. 70, nearly balances the  $\text{C}_3\text{Cl}$  group, m.w. 71.5.<sup>641</sup>

A 6-mercaptopyrimidine may be obtained by the hydrolysis of the isothiuronium salt from the 6-chloropyrimidine and thiourea. 6-Mercapto-2-alkylmercapto- compounds have been made similarly.<sup>585a</sup> 2-Chloro-4-(2-chloroethylamino)-5-nitropyrimidine and thiourea yield the thiuronium salt which is hydrolyzed to the 2-mercapto derivative. This can be cyclized to 1,4',5,6-tetrahydro-2-mercapto-4-methyl-5-nitroglyoxalinopyrimidine.<sup>599</sup> A solution of thiourea added dropwise to 5,5-dibromo-barbituric acid produces 5-amidinothio-2,4,6-trihydroxy-pyrimidine. 6-Amino-5-bromo-2,4-dihydroxypyrimidine in boiling ethanol treated with thiourea and then refluxed for 25 hours yields 5-amidinothio-6-amino-2,4-dihydroxypyrimidine.<sup>62</sup>

1-Methyl thiourea condenses with ethyl cyanoacetate to yield 4-amino-6-hydroxy-2-mercapto-3-methylpyrimidine.<sup>705</sup> Diphosphorous pentasulfide and 2-mercapto-4-hydroxy-6-methylpyrimidine heated at 160–170°C give 2,4-dimercapto-6-methylpyrimidine.<sup>734</sup>

Ethyl aminoacetate and carbon disulfide give the thiourea,  $\text{SC}(\text{NHCH}_2\text{CO}_2\text{Et})_2$ , which condenses to 2-thio-5-keto-4-car-

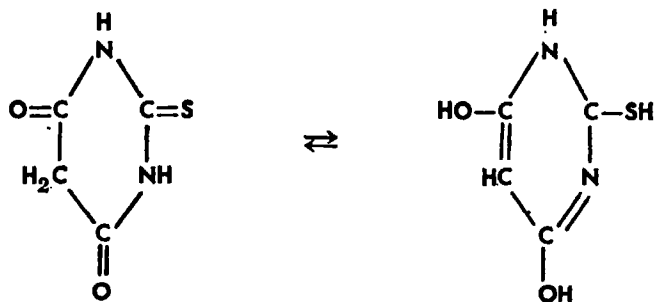
bethoxy-hexahydro-pyrimidine, m. 275°, a sensitive reagent for silver ions.<sup>656, 774</sup>

2-Mercapto-5-hydroxy-4-carbethoxy-1,3-dihydropyrimidine has been made starting with carbon disulfide and ethyl  $\alpha$ -aminoacetate.<sup>774</sup> 5,6-Diamino-4-hydroxy-2-mercaptopyrimidine and 4,5,6-triamino-2-mercaptopyrimidine have been prepared by reduction of the corresponding alloxan derivatives.<sup>703</sup>

Ethyl amine refluxed with 2-methyl-2-isothiocyano-4-pentanone yields 2-mercapto-1-ethyl-4,4,6-trimethyl-1,4-dihydropyrimidine.<sup>491</sup>

4,5,6-Triaminopyrimidine treated with aqueous sodium dithioformate yields 4,6-diamino-5-thioformamidopyrimidine.<sup>50a</sup>

Attention should be called to the isomerism between thiobarbituric acid and 2-mercapto-4,6-dihydroxypyrimidine:



This isomerism is possible when there is a single substituent in the 5-position but not when there are two, and not when there is an alkyl on the sulfur. There is similar isomerism with dithio- and trithiobarbituric acids and the dimercapto- and trimercaptopyrimidines. Reference should be made to Chapter 4 of Volume V on *Thiobarbituric Acid*.

## REACTIONS

### Desulfurization

Desulfurization may be accomplished in various ways. Raney-nickel replaces the —SH group of 4-hydroxy-2-mercapto-5-methoxypyrimidine with hydrogen.<sup>464</sup> The 4-hydroxy-2-mercapto-6-phenyl pyrimidine is desulfurized to 4-oxo-2-imino-6-phenyl tetrahydropyrimidine by heating with alcoholic ammonia.<sup>729</sup> 4,6-Dioxo-2-thio-5,5-dimethyl hexahydropyrimidine on treatment with hydrogen peroxide in hydrochloric acid yields 5,5-dimethyl-

barbituric acid.<sup>240a</sup> Dimethylmalonic acid amide is formed from the same compound on treatment with sodium amalgam in water.<sup>225</sup> Heating 6-oxo-4-imino-2-thio-5,5-dimethylhexahydropyrimidine with acetic acid gives 5,5-dimethyl-barbituric acid;<sup>240a</sup> with hydrochloric acid only the imino group is replaced to leave the thiobarbituric acid.<sup>240d</sup> 6-Phenyl-uracil is produced when 4-hydroxy-2-mercapto-6-phenylpyrimidine is heated with chloroacetic acid.<sup>371</sup> 2-Hydroxy-4-methylaminopyrimidine is prepared from 2-mercapto-4-methylaminopyrimidine and chloroacetic acid.<sup>110d</sup> Thiobarbituric acid is converted to 2-(3-diethylaminopropylamino)4,6-dihydropyrimidine by refluxing it with diethylaminopropylamine and lead hydroxide is isoamyl alcohol.<sup>405</sup>

### Other Reactions

Treatment of 6-mercapto-2,4-dimethylpyrimidine with alkaline potassium iodide gives bis-[2,6-dimethylpyrimidyl (4)]-disulfide.<sup>640</sup>

Heating the sodium salt of 6-amino-5-formamino-4-hydroxy-2-mercaptopyrimidine at 250–55° yields 6-hydroxy-2-mercaptapurine. At 230°, the potassium salt of 4,6-diamino-5-formamino-2-mercaptopyrimidine decomposes to give a 6-amino-2-mercaptapurine.<sup>703</sup> Refluxing 4,5-diamino-2-mercaptopyrimidine in formic acid for three hours yields 2-mercaptapurine.<sup>11</sup>

The isonitroso group of 4-amino-5-isonitroso-2-thio-6-hydroxypyrimidine is reduced to the amino group by sodium dithionite.<sup>39a</sup> 4,6-Diamino-2-mercaptopyrimidine treated with aqueous sodium nitrite at 0° gives the 5-nitroso-derivative which is reduced by  $\text{Na}_2\text{S}_2\text{O}_4$  to 4,5,6-triamino-2-mercaptopyrimidine.<sup>83</sup> A 5-nitroso-thiopyrimidine may be reduced to the corresponding amino compound by sodium hydrosulfide,<sup>33</sup> sodium thionite,<sup>619a</sup> or zinc dust and acetic acid.<sup>255, 375</sup>

By treating a 5-nitroso-thiopyrimidine with sodium dithioformate, the 5-nitroso group is transformed to the thioformamido.<sup>334, 453</sup>

Complex salts are obtained from mercaptopyrimidines which contain salt-forming groups such as  $\text{RHN}-$  and  $-\text{CO}_2\text{H}$  by treatment with salts of silver, gold, copper, or other heavy metals.<sup>342, 343</sup>

## Alkylmercaptopyrimidines

### PREPARATION

As mercaptans, mercaptopyrimidines can be alkylated by an alkyl halide in the presence of alkali.<sup>382a, 386a, 738c, 741a</sup> As alkylating agents the following have been used: methyl iodide<sup>478, 691</sup> or sulfate,<sup>691</sup> benzyl chloride,<sup>229</sup> ethyl chloracetate,<sup>188c, 508</sup> phenacyl chloride,<sup>188d</sup> and chloroacetamide.<sup>188b</sup> With ethyl bromide or iodide and alkali an ethyl group is put on the sulfur atoms of these compounds: 4-hydroxy-6-methyl-5-benzyl-,<sup>741a</sup> 4-hydroxy-5-phenoxy-6-phenoxyethyl-, and 4-hydroxy-5- $\beta$ -naphthoxy-6- $\beta$ -naphthoxyethyl-<sup>373</sup> 2-mercaptopyrimidines.

The alkylmercapto derivatives may be formed directly from the chloropyrimidine and a sodium mercaptide<sup>48a, 104, 204, 296, 552, 620, 688</sup> or from the iodopyrimidine and a copper mercaptide.<sup>120</sup> Under the same conditions dichloropyrimidines give di(alkylmercapto)pyrimidines.<sup>204</sup> 6-*p*-Nitrophenylmercapto-2-amino-4-methylpyrimidine resulted when 2-amino-4-methyl-6-chloropyrimidine was treated with *p*-nitrothiophenol.<sup>241</sup>

S-Alkyl thioureas may be used as starting materials.<sup>659</sup> 2-Methylmercapto-6-carboxyl-5-methyl-4-hydroxypyrimidine has been made from the condensation of S-methyl thiourea with the sodium salt of diethyl oxalpropionate,<sup>358b</sup> and 2-ethylmercaptopyrimidines from the condensations of S-ethylthiourea with EtO<sub>2</sub>CHC(OEt):CH·ONa,<sup>378b</sup> diethyl acetone carboxylate,<sup>740c</sup> sodium diethylmethyl oxalacetate,<sup>379</sup> diethyl ethoxymethylene malonate,<sup>739</sup> the sodium salt of formyl carbethoxyaminoethyl acetate,<sup>358b</sup> the sodium salt of carbethoxy malonic aldehyde,<sup>223</sup> and EtOCH:C(CO<sub>2</sub>Et)<sub>2</sub>.<sup>364</sup> S-Methyl isothiuronium iodide<sup>427a</sup> and sulfate,<sup>94b, 150, 313a, 466a, 674, 772</sup> and the S-benzyl chloride<sup>159, 208, 683</sup> have been used similarly. 2-Methyl-4-amino-5-pyrimidylmethyl chloride reacts with thiourea as an alkyl halide to give an isothiuronium salt.<sup>634, 636</sup> This product is not strictly a thio-pyrimidine.

Substituted 2-(carboxymethylmercapto)pyrimidines have been prepared by heating 4-amino-2-mercapto-pyrimidines with chloroacetic acid. Some others prepared were: 4-amino-6-methyl-, 4-tetradecylamino-, 4-benzylamino-, 4-(1-piperidyl)-, 4-(4-Methylpiperazino)-, 4-anilino-, 4-anilino-5-methyl-, 4-

anilino-6-methyl-, and 4-anisidino.<sup>323a</sup> 2-Mercapto-4,6-diaminopyrimidine and the ethyl ester of chloroacetic acid give ethyl (4,6-diamino-2-pyrimidylmercapto) acetate.<sup>188c</sup>

The reaction of ethyl mercuric chloride with 2-methyl-4-mercapto-5-pyrimidine carboxylic acid puts an EtHg-group on the sulfur atom.<sup>835</sup>

6-Benzylmercapto-2-dimethylamino-4-hydroxypyrimidine has been formed by heating benzyl mercaptan and 2-dimethylamino-4-hydroxy-6-aminopyrimidine with alkali in ethylene glycol at 150°. <sup>620</sup>

## REACTIONS

### *Alkylation*

2-Alkylmercaptopyrimidines can be alkylated further, on the two nitrogen atoms and also on the oxygen.<sup>365a, 370, 376b, 382b, 437</sup> 2-Ethylmercapto-5-ethoxy-4-hydroxypyrimidine is methylated on a nitrogen to give 1-methyl-2-ethylmercapto-5-ethoxy-4-hydroxypyrimidine.<sup>376b</sup> With the same reagent, 4-hydroxy-2-phenacylmercapto-6-methylpyrimidine is methylated similarly, but with ethyl bromide or with benzyl chloride the hydroxyl group is alkylated. With the corresponding 2-allylmercapto compound both types of alkylation take place with ethyl bromide.<sup>3</sup> Dimethyl sulfate puts a methyl group in the 1-position in 4-hydroxy-2-methylmercapto-6-amino-pyrimidine. Treatment with chloroacetamide converts the 2-SMe group of 4,6-diamino-2-methylmercaptopyrimidine to  $\text{—SCH}_2\text{CONH}_2$ .<sup>188a</sup>

A mixture of the 1- and 3-methiodides is obtained by treating 2-amino-4-methylmercapto-6-methylpyrimidine with methyl iodide.<sup>9</sup>

### *Reduction*

The oxime of 4,4-hydroxy-2-phenacylmercapto-6-methylpyrimidine is reduced by sodium amalgam to 6-methyl-2-thiouracil.<sup>382a</sup> The ethyl ester of  $\beta$ -hydroxy- $\alpha$ -[6-hydroxy-4-methylpyrimidyl-(2)mercapto]-acrylic acid is converted to S-[6-oxo-4-methyldihydropyrimidyl-(2)]-thioglycolic acid.<sup>386a</sup> Sodium in alcohol reduces 4-hydroxy-2-ethylmercapto-5-methylpyrimidine to 1,2-diamino-2-methylpropane and 2-ethylmercapto-1,4-dimethylpyrimidine-(6) to 3-amino-1-methylaminobutane.<sup>377c</sup> The 5-

carbethoxy groups of 2-ethyl<sup>211a, 516</sup> and 2-methyl<sup>711a</sup> mercaptopyrimidines are reduced to hydroxymethyl; and the 5-formamido-<sup>110c</sup> group of 4-amino-5-formamido-5-methylmercaptopyrimidine are reduced to the methyl amino by lithium aluminum hydride.

### Halogenation

Halogenation puts a halogen atom in the 5-position.<sup>68, 121, 129, 375, 377a, 735</sup> 4-Hydroxy-2-methylmercaptopyrimidine is brominated to 5-bromo-2-methylmercaptopyrimidone-4;<sup>377c</sup> 4-hydroxy-2-methylmercapto-6-amino-pyrimidine to 2-methylmercapto-4-oxo-6-imino-tetrahydropyrimidine;<sup>374a, 374b</sup> and 2-methylmercapto-4-amino-6-anilinopyrimidine to 5-bromo-2-methylmercapto-4-imino-6-[4-bromophenylimino]-tetrahydropyrimidine.<sup>374b</sup>

With phosphorus oxychloride chlorine was substituted for the hydroxyl groups of [4-hydroxy-2-methylmercapto-6-methylpyrimidyl-(5)]-acetic acid,<sup>372a</sup> 5-bromo-4-hydroxy-2-methylmercaptopyrimidine,<sup>377a</sup> 4-hydroxy-2-ethylmercapto-6-methyl-5-ethylpyrimidine,<sup>381</sup> the ethyl ester of 4-hydroxy-2-ethylmercaptopyrimidyl-(5) acetic acid,<sup>358b</sup> 2-ethylmercapto-5-carbethoxy-4-hydroxypyrimidine,<sup>737a, 737b</sup> and 2-methylmercapto-4-hydroxy-5,6-dimethyl pyrimidine.<sup>177</sup> The same reagent chlorinates 2-methylmercapto-5,6-dimethylpyrimidine in the 4-position.<sup>340</sup> Without being isolated the chloro compound can be used in a further synthesis.<sup>469</sup> Zinc dust removes the chlorine from a chlorinated alkylmercaptopyrimidine in boiling ethanol<sup>121, 483, 494b</sup> or in a benzene solution refluxed with water that contains sodium chloride and ammonia.<sup>494a</sup>

### Reactions with Amines

2-Ethylmercapto-5-methyl, 2-ethylmercapto-5-carbethoxy,<sup>737a</sup> and 2-ethylmercapto-4,5-dimethyl-6-chloropyrimidines<sup>146</sup> treated with alcoholic ammonia at 150° yield the corresponding 6-amino derivatives. 6-Chloro-2-ethylmercapto-4-aldehydopyrimidine is converted to 2-ethylmercapto-6-amino-4-iminomethylpyrimidine by alcoholic ammonia at 125°.<sup>381</sup> The same treatment at 170° substitutes imino groups for the alkylmercapto groups of the ethyl esters of 2-ethylmercapto-4-imino-dihydropyrimidine-car-

boxylic acid-(5)<sup>737a</sup> and [4-hydroxy-2-methylmercapto-6-methylpyrimidyl-(5)]-acetic acid.<sup>372a</sup> Refluxing [4-hydroxy-6-methylpyrimidyl-(2)-mercapto]-pyrrolic acid in an alcoholic solution of hydroxylamine puts an oximino group in place of the mercapto group. When 2-methylmercapto-5-methyl-4-hydroxypyrimidine is refluxed in an alcoholic solution of methylamine, the methylmercapto group is replaced by a methylamino group.<sup>386b</sup> When a 2-methylmercapto-4-hydroxy-6-methylpyrimidine is heated with diethylaminoethylamine the —SMe group is substituted by —NH(CH<sub>2</sub>)<sub>2</sub>NEt<sub>2</sub>.<sup>182</sup> A 4-methylmercapto group may be similarly substituted.<sup>180</sup> Refluxing 2-methylmercapto-4,6-dimethylpyrimidine and aniline puts —NHPh in the 2-position.<sup>185</sup>

4-Amino-6-methoxy-2-methylmercaptopyrimidine heated with bromine in acetic acid and treated with water and ammonia yields 2,4-diamino-5-bromo-6-hydroxypyrimidine.<sup>711b</sup> The chlorine in 2-methylmercapto-4-amino-6-chloropyrimidine may be substituted by —NMe<sub>2</sub>;<sup>20c, 52</sup> that in 2-methylmercapto-4-chloro-6-methylpyrimidine by *p*-ClC<sub>6</sub>H<sub>4</sub>NH—,<sup>183</sup> by *p*-acetamidophenylsulfonyl,<sup>585c</sup> or by —NHPh;<sup>8</sup> and that in 4-chloro-2-ethylmercapto-5,6-dimethylpyrimidine, by *p*-ClC<sub>6</sub>H<sub>4</sub>NH—.<sup>181b</sup> 4,6-Diamino-2-methylmercapto-5-nitrosopyrimidine and *N,N*-bis-(2-chloroethyl)-2-naphthylamine give 8-amino-6-methylmercapto-5,7,9,10-tetraazo-1,2-benzanthracene.<sup>242</sup>

### Desulfurization

Treating a 2-ethylmercaptopyrimidine with 30% hydrogen peroxide in absolute alcohol substitutes a hydroxyl group for the —SEt.<sup>144a, 144b</sup>

Alkylmercapto groups are removed by boiling with concentrated hydrochloric acid. From a number of 4-hydroxy-2-alkylmercapto-6-substituted pyrimidines the respective uracils have been obtained.<sup>372a, 373, 382b, 739, 740a</sup> Similarly, 2-ethylmercapto-4-alkylaminopyrimidines have been converted to the corresponding tetrahydropyrimidines.<sup>354b, 354c, 356a</sup> Boiling 4-methylmercapto-1,5-dimethyl-2-oxo-pyrimidine with dilute hydrochloric acid yields 3,5-dimethyluracil.<sup>741b</sup> 2,5-Di-*p*-tolyl-1,4-dithiin results from heating 4-hydroxy-2-*p*-tolacylmercapto-6-methylpyrimidine with 20% hydrochloric acid.<sup>383</sup> Under similar conditions 2-(*p*-

chlorophenylmercapto)-4-hydroxypyrimidine gives 80% of the uracil.<sup>238</sup>

Heating with ethanol and sulfuric acid esterifies the acetic acid group of [4-hydroxy-2-methylmercapto-6-methylpyrimidyl-(5)]-acetic acid and forms some 6-methyluracil-5-acetic acid.<sup>372a</sup> A similar reaction takes place with chloroacetic acid. 4-Hydroxy-2-ethylmercapto-6-methyl-5-ethylpyrimidine is converted to 5-ethyl-6-methyluracil,<sup>361</sup> while under similar conditions 2-thio-4-ethoxymethyl-5-ethoxy-6-ketopyrimidine is desulfurized to 5-hydroxy-6-hydroxymethyluracil.<sup>362</sup>

Hydrogen chloride removes the alkyl but not the sulfur: [6-oxo-2-ethylmercapto-pyrimidyl-(4)]-acetic acid is converted to 6-methyl-2-thiouracil<sup>740a</sup> at 170° and 4-mercapto-2-ethylmercapto-5-methylpyrimidine to 2,6-dithiothymine at 215°.<sup>741b</sup>

4-Hydroxy-2-phenacylmercapto-5-methylpyrimidine heated in acetic acid solution at 100° yields 6-methyl-2-thiouracil.<sup>382a</sup>

One experiment on the desulfurization of 2-methylmercapto-6-methyl-5-piperidinomethyl-4-hydroxypyrimidine is recorded, but the yield of the desulfurized product was only 10%.<sup>867</sup>

### Other Reactions

Treatment of the ethyl ester of S-[4-hydroxypyrimidyl-(2)]-thioglycolic acid with ethyl formate substitutes (:CHOH) for the hydrogens of the methylene group in the thioglycolic acid portion; and with oxalic acid one of these methylene hydrogens is substituted by  $\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ .

Warming the ethyl ester of  $\beta$ -hydroxy- $\alpha$ -[6-hydroxy-4-methylpyrimidyl-(2)-mercapto]-acrylic acid with thiourea in sodium ethylate solution produces [6-oxo-4-methyl-dihydropyrimidyl-(2)]-[4-oxo-2-thion-tetrahydropyrimidyl-(5)] sulfide.<sup>386a</sup>

The (2,5-dichlorophenylazo) group is introduced into the 5-position of alkylmercaptopyrimidines by treating the pyrimidine with 2,5-dichlorophenylazo chloride.<sup>403</sup> By treatment with copper sulfate, a 5-phenylazo-4-alkylmercaptopyrimidine has been converted to a triazole.<sup>309</sup>

Treatment with  $\text{Cl}_3\text{CCHO}$  converts the 2-amino group of 2-amino-4-methyl-6-methylmercaptopyrimidine to  $-\text{NHCH}(\text{OH})\text{CCl}_3$ .<sup>338</sup> The 5-amino group of 5,6-diamino-4-hydroxy-2-methylmercaptopyrimidine is changed to the thioureido group,

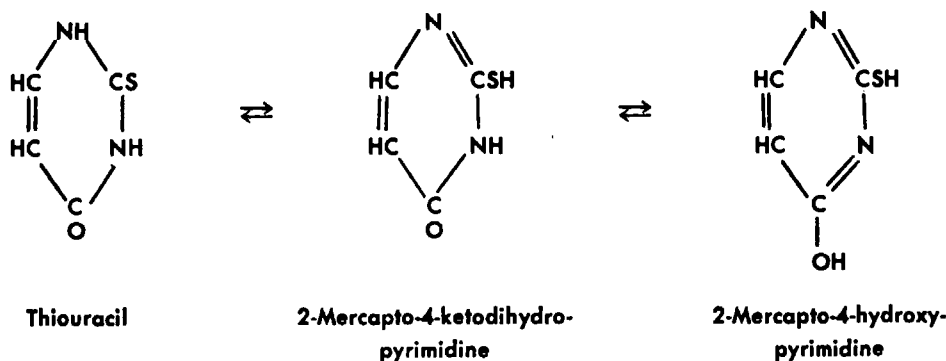


MeNH·CS·NH—, by methyl isothiocyanate.<sup>169</sup> The 4-amino group of 2-methylmercapto-4-amino-6-oxo-dihydropyrimidine is removed by treatment with nitrous acid, sodium dithionite, and formylamine.<sup>103</sup> 2,5-Diamino-4-allylmercaptopyrimidines may be diazotized.<sup>619a</sup>

Treatment of 2-methylmercapto-6-methyl-4-hydroxypyrimidine with formaldehyde and piperidine puts the piperidinomethyl group in the 5-position.<sup>667</sup>

The chlorine in 2-ethylmercapto-4-methyl-5-propyl-6-chloropyrimidine is substituted by —OR on treatment with sodium methylate or ethylate.<sup>147b</sup>

## Thiouracil



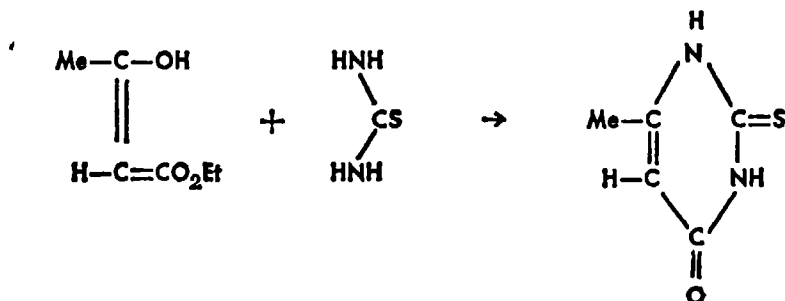
The most interesting of the 2-mercaptopyrimidines is the one that has a hydroxyl in the 4-position. This is known as *thiouracil*. The keto-thione formula is commonly written, though it may react as either of the other possible tautomeric forms. Hence, its chemistry is quite varied. Some of these 4-hydroxy-2-mercaptopyrimidines have already been considered in the previous section. Recently thiouracil and its alkyl derivatives have aroused interest on account of their physiological properties. The 6-methyl derivative is the most readily available and has, consequently, received the most attention.

## PREPARATION

Recent interest in the physiological effects of thiouracil derivatives has led to the synthesis of a host of these.<sup>25, 28a, 36a, 276, 348, 518, 582, 672</sup> some of which are listed in the table of properties.

The condensation of acetoacetic ester with thiourea was first

effected by Nencki and Sieber;<sup>546</sup> the constitution of the product was later established by Behrend.<sup>77, 444</sup> At first the condensing agent was hydrochloric acid, but sodium ethylate, or hydroxide, has been found more efficient; a combination of sodium sulfate and hydroxide has been recommended:<sup>415</sup>



The acetoacetic ester is written in the *enol* form. The condensation may take place with unisolated acetoacetic ester.<sup>425</sup>

As the result of a large number of experiments, the following method of preparation is given:

To a solution of 115 g dry sodium methylate (2 moles of 95%) in 900 cc anhydrous methanol are added to 130 g ethylacetoacetate (1 mole) and 76 g thiourea (1 mole). The mixture is refluxed on the steam bath for one hour and the methanol taken off at reduced pressure. The solid residue is dissolved in 250 cc cold water and filtered. The filtrate is acidified with dilute acetic acid to pH 5, warmed gradually to 80°, and then allowed to stand overnight. The almost-white precipitate is filtered off, washed free of acid, and dried at 110°. <sup>192</sup> The unmethylated 2-thiouracil is prepared from the less available formylacetic ester.<sup>424, 550, 619b, 669, 740c</sup> With ethyl-2-formylstearate, the product has the cetyl group in the 5-position.<sup>695</sup>

A large number of thiouracils having R in the 6-position have been prepared by condensing thiourea<sup>670</sup> with  $\beta$ -keto esters,<sup>386a</sup> in which R may be ethyl,<sup>615</sup> hexyl,<sup>722c</sup> amyl,<sup>773</sup> benzhydryl,<sup>441</sup>  $\alpha$ - or  $\beta$ -naphthyl, and  $\alpha$ - or  $\beta$ -naphthylmethyl.<sup>151</sup>

The acetal  $(\text{EtO})_2\text{CHCOCH}_2\text{COOEt}$  condenses with thiourea to form a 2-thiouracil with the  $(\text{EtO})_2\text{CH}-$  group in the 4-position.<sup>366b, 381</sup> This is hydrolyzed to 2-thiouracil-4-aldehyde, which by the Cannizzaro reaction, gives 2-thio-4-hydroxymethyluracil and 2-thioörotic acid.<sup>588</sup> 6-Diethoxymethylthiouracil, tagged in the 4-position, has been prepared from  $(\text{EtO})_2\text{CHCOCHNa}-$

C\*O<sub>2</sub>Et and thiourea.<sup>418</sup> Dihydro-6-methyl-2-thiouracil has been obtained by heating MeCH:CHCO<sub>2</sub>Et with thiourea in a sealed tube for ten hours.<sup>195</sup> The 3-substituted-5-carbethoxy-2-thiouracils are made by condensing the appropriate alkyl- or arylthiourea with EtOCH:C(CO<sub>2</sub>Et).<sup>745a</sup> The reaction rate of S-labeled thiourea with NaOCH:CHCO<sub>2</sub>Et has been studied.<sup>780</sup> The  $\alpha$ -propyl group of AcCHPrCO<sub>2</sub>Et goes in the 5-position.<sup>147a</sup> An  $\alpha$ -substituent, R', in the  $\beta$ -ketoester, RCOCHR'CO<sub>2</sub>Et, is found in the 5-position of the resultant thiouracil.<sup>36a, 39b, 146, 361, 362, 369b, 373</sup>

1,3-Di- $\beta$ -naphthyl-6-methylthiouracil is obtained from the dinaphthylthiourea and acetoacetic ester.<sup>588</sup> Phenyl isothiocyanate and ethyl  $\beta$ -aminocrotonate unite to give 3-phenyl-6-methylthiouracil.<sup>78</sup> Ethyl cyanoacetate and thiourea condense to 6-aminothiouracil.<sup>703, 717</sup> An acylthiourea is formed by the reaction of a  $\beta$ -cyano-ester in the presence of sodium ethylate:<sup>508</sup>



This may be considered as the first step in the condensation to 6-imino-5,5-diethyl-6-keto-dihydro-2-thiouracil. The condensation is usually carried through without isolating the intermediate. Many compounds of this type have been prepared.<sup>168, 240a, 508, 703, 705</sup> Hydrolysis of the imino group gives a thiobarbituric acid.<sup>168, 240a</sup>

Ethyl  $\beta$ -thiuraminocrotonate, heated with sodium ethylate, is transformed to 6-methylthiouracil.<sup>107</sup> The same compound is obtained from  $\beta$ -aminocrotonic ester and phenylisothiocyanate.<sup>78</sup>

6-Amino-5-bromouracil treated with sodium disulfide yields di(6-amino-2,4-dihydroxy-5-pyrimidyl) disulfide. A similar disulfide is obtained from 6-amino-5-bromo-1-methyluracil, but not from 5,5-dibromohexahydro-6-imino-1-methyl-2,4-dioxo-pyrimidine and 5-bromouracil.<sup>61b</sup>

## REACTIONS

### *With Metal Salts*

Thiouracil and its 6-methyl derivative give precipitates with copper sulfate.<sup>442.5</sup> 6-Methyl-2-thiouracil acts as a dibasic acid, forming salts with many metals. The alkali and ammonium salts are formed by direct neutralization, the heavy metal salts by

precipitation. Some of these are  $C_5H_4N_2OSAg_2$ ,  $C_5H_4N_2OSCu$ , and  $(C_5H_5N_2OS)_2Hg$ . The potassium salt is only slightly soluble in water, only 0.54 g in one liter of water at  $21^\circ$ .<sup>444</sup> The addition of dilute solutions of soluble heavy metal salts to aqueous saturated solutions of 6- and 5-substituted thiouracils caused partial ( $Zr^{+2}$  and  $Fe^{+2}$ , 5%;  $Mn^{+2}$ , 10%), or complete ( $Cu^{+2}$ ) precipitation of the thiouracil through formation of chelate complexes.  $Co^{+2}$  yields no precipitate. The complex ion involves one atom per molecule of thiouracil and the speed of formation depends on the nature of the thiouracil uses.<sup>439a</sup>

### Hydrogenation

Dihydro-4-methyl-2-thiouracil is prepared by hydrogenating 4-methyl-2-thiouracil with Na/Hg amalgam.<sup>195</sup> Reduction of a thiouracil by sodium in ethanol breaks the ring on both sides of the 2-carbon atom, giving a mercaptan and a trimethylene diamine.<sup>377c</sup>

### Oxidation

2-Thiouracil is oxidised by iodine to the disulfide;<sup>164, 614</sup> so is its 4-(2-furyl)-derivative.<sup>28a</sup> In a phosphate buffer, 4-thiouracil is oxidised by iodine to the disulfide, m.  $223^\circ$ .<sup>614</sup> Nitric acid removes the sulfur from 4-ethyl-2-thiouracil leaving 4-ethyluracil.<sup>615</sup> The sulfur of a thiouracil is converted to the sulfate ion quantitatively by hydrogen peroxide.<sup>408</sup>

Bromine in acetic acid solution produces 5-bromo-2-thiobarbituric acid imide-(4) from 4-amino-2-thiouracil.<sup>168</sup> 3-Methyl-4-amino-2-thiouracil is changed to 1-methyl-barbituric acid imide-(6).<sup>705</sup> 4-Phenyl-2-thiouracil is desulfurized by treatment with  $SbO_2$ -HOAc to 4-phenyluracil.<sup>529b</sup> Thiouracils have been desulfurized by Raney Nickel.<sup>95, 111, 236, 576, 609</sup>

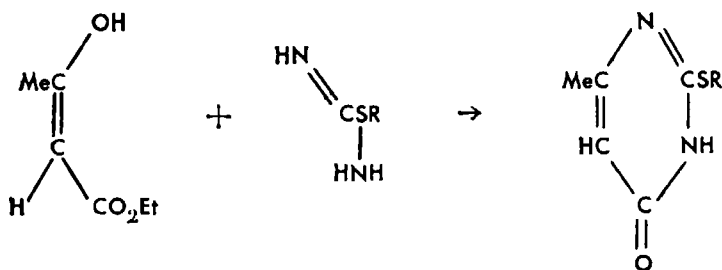
### Alkylation

2-Thiouracil and its derivatives can be alkylated by treatment with alkyl halides in alkaline solution. The thiouracil reacts as the alkali salt of its tautomeric mercapto form and the product is a 2-alkylmercaptopyrimidine.<sup>68, 146, 276, 330, 369b, 373, 377a, 382a, 385, 386a, 740a</sup>

2-Hydroxy-4-methylmercapto-6-methyl-pyrimidine results

from the treatment of 4-methyl thiouracil with methyl iodide in alcoholic alkali.<sup>741a</sup> With chloroacetic acid, a  $-\text{CH}_2\text{CO}_2\text{H}$  group is added to the sulfur atom of 1-methyl-5-hydroxy-2-thiouracil.<sup>376b</sup> 2-Thio-4-methyluracil, 6-methyl-5-( $\beta$ -hydroxyethyl)-2-thiouracil, 4-methyl-5-ethyl-2-thiouracil, and 5-alkyl derivatives of 4-methyl-2-thiouracil are converted to the corresponding alkylmercaptopyrimidines by treatment with methyl iodide,<sup>401</sup> or sulfate,<sup>649</sup> or ethyl bromide<sup>147c</sup> in alkaline solution. Ethyl-(6-hydroxypyrimidine-2-thioglycolate is obtained similarly from ethyl chloroacetate and 2-thiouracil.<sup>386a</sup>

Similar products can be obtained by condensing the appropriate alkylisothiuronium salts,  $\text{RSC}(:\text{NH})\text{NH}_2\cdot\text{HX}$ , with  $\beta$ -keto- or formyl esters:



An excess of sodium ethylate is used to take care of the acid of the salt. These have been prepared in great number and variety.<sup>223, 330, 354a, 358b, 359, 364, 372a, 378b, 379, 380, 735, 739, 741b, 742</sup> The hydroxymethyl group,  $\text{HOCH}_2-$  is introduced into the 5-position in 4-methyl-2-thiouracil by formaldehyde and hydrochloric acid.<sup>581, 607</sup> In concentrated hydrochloric acid, this product is reduced by tin to 5,6-dimethyl-2-thiouracil, m.  $275^\circ$ .<sup>607</sup>

### Halogenation

A thiouracil can be halogenated indirectly. It is alkylated on the sulfur to the 2-SR which is halogenated in the 5-position. The alkyl is then removed from the sulfur by anhydrous hydriodic acid.<sup>68</sup> The 2-ethylmercapto- is iodinated in the 5-position by iodine and alkali.<sup>374a</sup> Chloro derivatives are obtained from hydroxy thiouracils by treatment with phosphorus oxychloride,<sup>147c</sup> or phosphorus pentachloride.<sup>738a</sup> Alkylated thiouracils may be chlorinated by sulfur chloride or chlorine in the presence of ferric chloride.<sup>66</sup> 1-Allyl-4-methylthiouracil treated with 20% bromine

in acetic acid and diluted with water gives  $\overline{\text{CO}\cdot\text{CH}\cdot\text{CMe}\cdot\text{N}\cdot\text{C}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CBr}(\text{CH}_2\text{Br})\cdot\text{S}}$ .<sup>274</sup>

### Other Reactions

2-Thio-4-methyluracil and *p*-dimethylaminobenzaldehyde refluxed in aniline for four hours yielded 2-thio-4-(*p*-dimethylaminostyryl) uracil.<sup>112</sup> The  $-\text{CH}_2\text{NHC}_6\text{H}_4\text{CO}_2\text{H}$  is introduced into the 5-position of 2-thio-4-methyluracil by treatment with 40% formaldehyde and *p*-aminobenzoic acid.<sup>529a</sup>

The dealkylation of 4-propyl-2-thiouracil is effected by heating with potassium hydrogen sulfide and two parts of ethanol.<sup>668b</sup> Boiling a 2-alkylmercaptothiouracil with aqueous hydrochloric acid splits off mercaptan leaving the corresponding uracil.<sup>78, 129, 359, 365a, 376b, 380, 444, 741a, 742</sup> With hydrobromic acid—or better with hydriodic—in glacial acetic acid, only the alkyl is removed, leaving a 2-thiouracil.<sup>365a</sup> Improved directions for this operation have been given.<sup>68</sup>

Sodium nitrite in acetic acid substitutes the oximino group for the hydrogen in the 5-position of 3-methyl-4-amino-2-thiouracil, and the resulting compound is 1-methyl-4-oxo-6-imino-5-oximino-2-thion hexahydropyrimidine.<sup>705</sup>

Heating 3-methyl-2-methylmercapto-5,6-diamino pyrimidone-(4) with thiourea at 160–170° yields 1-methyl-6,8-dihydroxy-2-methylmercaptapurine.<sup>356b</sup>

### ESTIMATION

Thiouracil and its derivatives are determined colorimetrically by the use of Grote's reagent, which was originally proposed for thiourea. The reagent is prepared by treating sodium nitroprusside in sodium bicarbonate with hydroxylamine and then with bromine. The excess of bromine is removed by aeration.<sup>293</sup> It has been found preferable to take care of this bromine by adding phenol. The color is measured at 580 mμ. Buffering at pH 6 is recommended.<sup>141</sup> This reagent, which is sensitive to compounds containing the grouping  $-\text{NH}\cdot\text{CS}\cdot\text{NH}-$  has been adapted to the determination of thiouracil and its derivatives in biological materials such as serum, blood, and urine.<sup>24, 190, 272, 328, 533, 553, 564a, 751</sup> The accuracy of the method and its adaptability to the determination of thiouracil and of several of its derivatives have been

tested.<sup>155</sup> It has been useful in following the excretion of thiouracil after it has been administered.<sup>24, 768</sup>

The thiouracil is removed from serum by dialysis<sup>386a</sup> or filtration.<sup>553</sup> Ultrafiltration has been recommended,<sup>155</sup> which may be through cellophane under moderate pressure.<sup>190</sup> Serum can be previously deproteinized by acid.<sup>155</sup> Thiouracil may be liberated from blood by tryptic digestion.<sup>751</sup>

Sodium ferricyanide may be used in the colorimetric determination of thiouracil.<sup>540</sup> A method of extracting with acetone and titrating in the presence of silver nitrate has been proposed.<sup>126</sup> A biological method depends on the use of radioactive iodine.<sup>258</sup> Pyrimidines substituted in the 2- and 5-positions by OH, NH<sub>2</sub>, or SH may be classified by the color produced with aqueous I<sub>2</sub>/KI.<sup>414</sup> Another colorimetric method of determination employs an isopropylamine reagent, which gives a band at 530 mμ.<sup>329</sup>

Volumetric methods have been proposed.<sup>1, 763</sup>

### Dithiouracils

Heating uracil or 2-thiouracil, with a phosphorus sulfide in Tetralin to 160–80° converts it to 2,4-dithiouracil. By the same treatment, only one sulfur atom is introduced into 1,3-dimethyluracil and that is in the 4-position.<sup>227a, 321a, 734</sup>

6-Methyl-2-methylmercapto-4-chloropyrimidine and potassium hydrosulfide give 6-methyl-2-methylmercapto-4-thiopyrimidine which can be demethylated to 6-methyl-2,4-dithiouracil.<sup>77</sup> 2,4-Dichloropyrimidine and potassium sulfide,<sup>368, 740c</sup> or hydrosulfide,<sup>368, 495, 740c</sup> give 2,4-dithiouracil.

Phenyl isothiocyanate reacts with ethyl orthoformate to give 1,3-diphenyl-6-ethoxy-2,4-dithiouracil.<sup>745b</sup>

Heating a 5-alkyldithiouracil with ammonia, methylamine, or piperidine substitutes —NH<sub>2</sub>,<sup>117b</sup> —NHMe,<sup>323b</sup> or —N(CH<sub>2</sub>)<sub>5</sub>,<sup>323c</sup> respectively, for the sulfur in the 4-position. Dithiouracils may be desulfurized by Raney-nickel.<sup>95, 160</sup>

### **Physiology of Thiouracil**

by

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The physiological effects of thiouracil and its several derivatives have been studied extensively, particularly with reference to the thyroid gland. A survey of biological, medical, and related literature (from 1907 to 1960) produced over 800 references—too much to treat adequately in this short review. The references cited are representative of important works leading to the mode of action of thiouracils with unusual changes, and are cited from animal, bacteriological, botanical, and human test systems without over-duplication.

There are several reviews on thiouracil, its action, and its therapy, with references running into the hundreds.<sup>41, 42, 87, 193a, 193c, 244, 393, 537a, 699</sup> These should be consulted for full information. At times the literature does not distinguish between thiouracil and its several derivatives, particularly the 6- or 4-methyl derivatives, as well as others.

Several hundred chemicals have been tested in animal systems for antithyroid properties—the ability of a compound to lower the iodine content of the thyroid<sup>456</sup>—with good success in a few cases. Chemical structure and position of substitution are important for qualification; see Table 2.1 for partial listing.

Some compounds listed have effects other than their effect on the thyroid gland. To counter thiouracil compounds, other chemicals (not from thyroid or pituitary, nor from the hormones) have been tested, and a few have been found acceptable (see Table 2.2 for partial listing). These chemicals have affected tissues other than that of the thyroid. Other compounds of both types are to be found in the following references: 39.5, 59, 67, 392a, 433, 439d, 456, 458, 476, 607, 647, 714, 758

Thiouracil has been found to inhibit the formation of the thyroid hormones (thyroxine, thyrotropin, etc.) and thereby the function of the gland.<sup>4, 32, 38, 101, 133, 152a, 153, 173, 197, 203, 277, 279b, 288, 326, 392b, 431, 432, 443, 449, 462, 486, 511, 519, 532, 563, 594, 603, 606, 645, 652, 655,</sup>



665, 721, 722a, 722c, 756, 766a The guinea pig and dog, however, do have certain differences, both being less dependent on the thyroid gland under certain conditions.<sup>38, 191, 279b, 391, 462, 519, 532</sup> There is usually definite increase in size and weight of the gland,<sup>73, 197, 243, 279a, 281, 288, 326, 432, 519, 594, 645, 648, 657.5, 721, 779</sup> with corresponding changes in tissue structure, which result in hyperplasia, or hypertrophy, of the gland.<sup>2, 3, 32, 101, 152a, 173, 214, 218, 244, 264b, 279a, 279b, 280, 288, 390, 392b, 409, 431, 486, 523, 563, 570.5, 594, 655, 721, 722a, 722b, 722c, 722d, 722e</sup> The guinea pig offers a complex to the normal findings.<sup>277, 285, 392b, 462</sup>

The mechanism of the action of thiouracil has been studied, and it appears to prevent the gland from utilizing iodine (inorganic or organic) for the formation of thyroxine; radioactive iodine has played an important part in these experiments, as found in the following references: <sup>12, 30, 31, 39.7, 63b, 98, 173, 218, 219, 253, 260, 277, 279b, 283, 288, 409, 432, 443, 455, 459, 460, 462, 500, 509, 566, 573, 603, 632, 700, 721, 722c, 765, 766a, 766b, 766d, 768, 771</sup> The colloidal nature of the gland has also been studied for its ability to accumulate or discharge iodine under various conditions.<sup>63b, 98, 173, 218, 409, 728b, 756</sup>

The ratio of the concentration or content of thyroid iodine (thyroid-protein-bound iodine, TPBI) to the concentration or content of serum iodine (serum-protein-bound iodine, SPBI) provides a measure of thyroid-to-thyroxine synthesis which thiouracil interrupts; it does show that where formation of thyroxine is active by repressal, the TPBI/SPBI is diminished under most conditions.<sup>32, 96, 98, 279b, 509, 690, 765, 766b, 766c</sup> Maloof<sup>473</sup> does present a conflict because he finds no serum-thyroid concentration gradient that holds consistently. A referral to radioactive iodine experiments also offers evidence of this ratio (TPBI/SPBI).

Other evidence of thyroid malfunction is obtained by transplanting whole or partial thyroid glands of treated animals into the abdominal cavity of tadpoles or near their tail. This technique shows that tadpoles so treated do not complete their metamorphosis and become oversized.<sup>38, 133, 152a, 152b, 394, 395, 721, 728a</sup> The hypophysis (dried) of thiouracil-treated rats, when injected into guinea pigs and young mice, resulted in maturation of follicles only without luteinization and estrus.<sup>417a</sup> Thyroid hyperplasia was induced in normal rats by a diet including ground fetuses from pregnant female rats that had been treated with thiouracil.<sup>264a</sup>

Thyroid hyperplasia—hypertrophy—as a result of thiouracil

and its derivatives can be countered by the hormone produced normally by the pituitary (within certain limits of concentration) and thyroid glands.<sup>96, 98, 197, 264b, 594, 618, 645, 721, 728b</sup> There is a similar action between thyrotropic hormone and thiouracil if the former is over concentration limits.<sup>98, 731</sup> When given together to guinea pigs, there is greater goitrogenic activity than from thiouracil alone;<sup>749</sup> but in the chick and pigeon the combination lowered the activity of the thyroid gland<sup>722c, 722d</sup>—a definite species difference. Experiments show also that when thiouracil and its derivatives are withdrawn there is a return of normal thyroid function.<sup>31, 32, 288, 392b, 457</sup>

Testosterone, growth hormone, methylestrone, and other androgenic estrogenic hormones have been used with varying success in preventing hyperplasia of the thyroid.<sup>275, 434a, 722e, 756, 771</sup> Vitamins B<sub>12</sub> and A also have beneficial effects against thyroid hyperplasia.<sup>171, 438, 501, 548, 682</sup>

Thiouracil and its derivatives can produce tumors in thyroid and other tissues and these appear to be transplantable to other test systems.<sup>524, 525, 537a, 537b, 539</sup> A thyroid histology suggestive of *Struma Lymphomatosa* was produced in rats on thiouracil,<sup>161</sup> and rats treated with propylthiouracil were successfully used to distinguish between Basedow syndrome patients and para-Basedow patients.<sup>612</sup> Studies of the functioning of the thyroid in relation to *d*,1-tyrosine, diiodotyrosine, thyroxine, some thyroidenzyme concentration, and thyroidectomy are to be found in many references: 81, 259, 409, 426a, 520, 566, 573, 625b, 715a, 766a, 777

The pituitary gland has a great influence on thyroid and other bodily functions. A large number of the references cited could be repeated in this and other sections; however, it is understood that all the literature cited will be restricted to references that mention specific changes in the gland or tissue described.

Thiouracil and its derivatives have caused increase in the size, number, and activity of the basophilic cells of the hypophysis, leading to a pituitary pathology similar to a thyroidectomy.<sup>434b, 486, 507, 569, 658, 721</sup>

Dose, length of time (on thiouracil drug), order of injection (of a hypophysis extract relative to the drug), and the drug given with other propensiating compounds appear to have direct relationships to hypothalamic-hypophysis damage and pituitary activity.<sup>13, 55, 99, 431, 662, 687, 721</sup>

Bilateral electrolytic lesions in hypothalamic regions were produced by propylthiouracil.<sup>99</sup> An unexpected result was that the pituitary failed to demonstrate uptake of radioactive iodine 131.<sup>397</sup> A hypophysis, rendered pale from methylthiouracil, was partially corrected by vitamin A, whereas cortisone and deoxycorticosterone opposed the morphological effects produced by each other.<sup>275, 548</sup> The thymus, when on thiouracil compounds, appears to be a more sensitive indicator to biological stress; the parathyroids showed changes, in some cases, similar to those in thyroid.<sup>48, 231, 472, 647</sup> The liver being the major organ of metabolism, detoxification, and synthesis, does show changes directly attributable to thiouracil compounds. In experiments on intact animals there is an increase in both the size and the weight of the liver through infiltration of fatty tissue, but there is a question about an increased rate of detoxification.<sup>1, 26.5, 89, 592</sup> A disagreement about damage to tissue in the liver by thiouracil is found in the following references: <sup>26.5, 300, 349, 471, 510</sup> The rate at which deuterium is incorporated from heavy water into liver steroids, protein, and glycogen is reduced by treatment with thiouracil. The content of glycogen is also significantly reduced.<sup>220a, 221, 399</sup>

In partial hepatectomies, thiouracil or its derivatives increased the rate of regeneration in the liver, and also showed an increase in the content of sulfhydryl groups in the liver.<sup>273, 333, 484, 485a</sup> Certain of these thiouracil compounds increased the level of crude protein in the liver, as shown by a higher phosphorus content of both desoxyribonucleic and pentose-nucleic acids in the liver, and a lower phospholipid content.<sup>166, 252, 477b</sup> Hyperthyroid rats on thiouracil showed higher values for nucleic acid in the liver, and hypothyroid rats showed lower levels. It has been reported that thiouracil compounds have a preventive effect in certain cirrhosis-producing diet; and also inhibit the formation or growth of certain types of tumors produced by fluorine compounds. This is effected either by competitive inhibition (a type of detoxification) or by cellular change—protection by thiouracil.<sup>127.5, 162, 295, 297a, 297b, 298, 565a, 565b</sup> It was found that uracil was still incorporated into liver nucleic acid, even though it counteracts the protective effect of thiouracil on the cells of the liver.<sup>127, 565c</sup> Unilaterally nephrectomized rats treated with propylthiouracil showed a rise in liver riboflavin, significant of

a reduced rate of excretion; and other experiments indicate that rats treated with thiouracil can convert  $\beta$ -carotene into vitamin A.<sup>402, 597, 747</sup>

A "chemical thyroidectomy"—from large doses of propylthiouracil—increased the Fe 59 content of the liver.<sup>44</sup> Thiouracil or its derivatives decreases the activity of enzymes in the liver—succinic oxidase, cytochrome oxidase, and both acid- and alkaline glycerolphosphatase.<sup>499, 700</sup> In experiments with hamsters, however, the concentrations of acid- and alkaline phosphatase and of catalase were increased.<sup>423, 598, 676</sup> From experiments with C 14, synthesis of cholesterol in the liver does not appear changed significantly.<sup>215</sup>

In a time study, rats treated with methylthiouracil showed reduced elimination of I 131 in the bile and volume of bile. Thyroidectomized dogs had increased excretion.<sup>413, 514</sup> Additional studies of liver function can be found in the following references: 82, 291, 411, 489, 496, 515

The pancreas has a major regulatory role in the conversion of glucose to glycogen (liver tissue primarily and to some degree in muscle tissue) through its synthesis and release of insulin. Experiments on intact animals indicate definite damage to pancreatic tissue where thiouracil compounds have been administered. Loss of granulation in the  $\beta$ -cells appears to be related to reduced synthesis or activity of insulin, but changes in  $\alpha$ -cells have not shown definite changes in activity of insulin.<sup>16, 631</sup> Thiouracil-treated animals were found increasingly resistant to diabetes induced by alloxan particularly in thyroidectomized rats; however, 40% of a group of 95% depancreatized rats had no evidence of diabetes and little change in the remaining morphology of  $\beta$ -cells.<sup>331, 332a, 332b, 485b</sup>

The animal test system used (dog, rabbit, and rat), its degree of thyroid function, and the sequence of administering thiouracil and insulin in experiments with alloxan resulted in interesting changes. Some dogs overcame the action of alloxan without insulin, whereas rabbits showed a quicker onset and a prolonged hypoglycemic response with insulin, and rats maintained their general deposits of body glycogen.<sup>171, 172, 556, 557</sup> Additional pancreatic-thiouracil changes are to be found in the following references:<sup>34, 605</sup>

The literature reports some cases of increase in both weight and

size of the adrenal gland and its medulla in animals treated with thiouracil compounds.<sup>220a, 220b, 480</sup> Other reports state a reduction in weight of the adrenals with corresponding reductions in the output of 17-keto- and corticosteroids; this condition is returned to normal by thyroxine.<sup>156, 419, 420, 421, 422</sup> The adrenal cortex has shown areas of hemorrhage, necrosis, severe congestion, and reduction to one-half its usual size; but, there are conflicting reports concerning the lipid content of the cortical zones in the adrenals.<sup>72, 139, 279a, 447, 510, 664, 778</sup> The dog does not show all of these changes, but young rats born of thiouracil-treated females showed partial atrophy of the adrenal cortex.<sup>279b, 766e, 776</sup> Atrophy of the adrenals is reported to be a specific action of thiouracil compounds, because rats so treated showed this atrophy, which was not overcome by vitamin B<sub>12</sub> supplement; (vitamine B<sub>12</sub> is known to retard the growth-inhibiting action of thiouracil).<sup>775</sup> Propylthiouracil, known to increase the ratio of thyroid-iodine to serum-iodine, appeared ineffective in rats with or without their adrenals; yet some rats, in comparison to other treated animals, had decreased content of adrenal ascorbic acid.<sup>262, 284, 571</sup>

The kidney of thiouracil-treated animals had an increased content of sulfhydryl groups, which was reduced when they were on alloxan, whether a subtotal or total pancreatectomy was performed.<sup>333</sup> Although some experiments on animals show little significant change in the kidneys, others definitely show evidence to hypertrophy, granular deposits in the kidney pelvis, varying degrees of damage to the tubes, and calcium deposits in the tubules.<sup>166, 248, 434b, 719</sup>

The activity of alkaline phosphatase and transaminase was reduced.<sup>500, 748</sup> Although propylthiouracil prevented an increase in blood pressure (where a kidney had been encapsulated with a latex envelope), methylthiouracil given with thyroxine showed little change in content of citric acid.<sup>263, 531</sup>

Thiouracil compounds affect the phenomena of reproduction, involving the male testes, the production of sperm, the female ovaries, and estrus cycle, finally resulting in transfer of these compounds through the placenta. The weight, size, and function of the testicles were reduced in male poultry birds. Though the production of sperm was not markedly affected, its time of survival was reduced.<sup>646, 651</sup> The weight of the ovary in females was reduced, with accompanying congestion and degeneration of the

Graafian follicles, which reduced the number of estrus cycles.<sup>63b, 278, 417b, 568</sup>

One investigator, however, challenges this by stating there is no definite reduction in the number of cycles nor any upset in the basic rhythm of the cycle.<sup>234</sup> Though there is no external change during the pregnancy of the guinea pig, a reduced flow of milk is evident; but rats born of treated female rats show varying degrees of hypothyroidism (varying with dose and time of gestation) definitely indicating transfer of the drugs through the placenta.<sup>15, 122, 163, 264a, 390, 400, 722a</sup> The new-born rats show marked retardation in growth (overcome somewhat by thyroxine), delay in appearance of ossification centers (dating from early days of pregnancy), and a modification in development of the central nervous system—delayed in cellular stratification.<sup>336, 513, 550, 732</sup>

The mammary glands of both male and female rats on thiouracil compounds show changes. Some investigators report hyperplastic cystic nodules in the mammary gland of the female rat with a possible increase in rate of secretion; whereas others find little or no change induced in the gland.<sup>135, 200, 234, 502, 666</sup> In new-born females from treated females, the estrus was inhibited or suppressed with a regressed mammary development; yet normal female rats gave signs of an increased liberation of estrogens by the ovaries, possibly through stimulation of the hypophysis.<sup>200, 213</sup>

Thiouracil-treated male rats and mice—both castrated—produced species differences when treated with diethylstilbestrol. Similarly treated guinea pigs and cocks (castrated and normal, and treated with methylstilbestrol) showed less hypertrophy of the thyroid gland because the steroid prevented loss of biological activity in the gland.<sup>706, 722e</sup> Testicular receptivity to gonadotropic hormone was increased by propylthiouracil, and chicks (on thiouracil and given P 32) had increased concentration of P 32 in their testes.<sup>174, 527b</sup>

Other related effects of thiouracil derivatives, hormones, and other compounds can be found in the following references:<sup>127.5, 165, 269, 270, 350, 644, 720, 757</sup>

Thiouracil-treated animals with inhibited thyroid function, were found to have cysts on their salivary glands and an increased number of dental caries.<sup>232, 247, 544, 570, 650</sup> New-born rats of non-treated females, given thiouracil compounds, exhibited

retarded eruption of teeth and opening of eyelids. This effect was reversed by simultaneous injection of desoxycorticosterone.<sup>562</sup> Small wounds of the corneal epithelium showed no delay in post-traumatic movement of cells, but the rate of tissue repair (mitosis and mitotic cycle) was reduced.<sup>250, 251</sup> The appearance of red pyknosis of the nucleus precedes hyperactivity of supra-optic neurons in rats treated with methylthiouracil; however, another investigator reports that the same compound was found to reduce the fatal outcome of nervous trauma, thus showing a reduced incidence of severe hemorrhage of brain tissue.<sup>207, 770</sup> Certain experiments on intact animals indicate circulatory change around the terminal vessels of the central nervous system (with changes between serum and marrow centers), which produce perivascular edema, without, however, any apparent change in the permeability of the walls of the vessel.<sup>300, 770</sup>

Arteriosclerotic vascular lesions in dogs were not generally evident in dietary experiments with thiouracil, though there was some increased deposit of fat in the aorta;<sup>64, 329, 677, 760</sup> other investigators gave conflicting evidence.<sup>541, 676.5</sup>

Thiouracil-treated animals showed changes in the spleen, ranging from increase in weight, nitrogen content, and nucleic acid content, to protection against destruction by ribonucleic acid, reduced turnover of Fe 59, and (in cases of splenectomized rabbits) and increased vascularity (leading to hemopoietic changes.)<sup>44, 189, 475, 515, 690</sup> Thiouracil produced pulmonary nodules of thyroid-like tissue but did not afford protection against pulmonary metastases that resulted from malignant tumors induced by thyrotropic hormones.<sup>288, 510, 538</sup>

Guinea pigs on methylthiouracil and thyroxine had a slight decrease in vitamin B<sub>12</sub> in the brain.<sup>531</sup>

Thiouracil compounds lower the rate and action of the heart in rats, but the opposite occurs in the frog; at reduced atmospheric pressures both dilantin and thiouracil increase time of survival with less extensive lung hemorrhage in the frog.<sup>14, 286, 289, 394, 511</sup>

Activity in bone marrow, as measured by production of leucocytes, granulation of reticulocytes, or oxidation of *p*-phenylenediamine, has been reported as increased, reduced, or without change.<sup>5, 392a, 288, 549a, 549b, 563, 566, 730</sup>

As a result of treatment with thiouracil, formation of pigment

was inhibited, and this was found directly related to the pigment granules in the melanoblast cells of chicks, as well as an enlargement of the tibia-metatarsal joint and its movement.<sup>106, 481</sup>

Metabolism in a normal functioning animal test system is changed, drastically at times, by thiouracil and its derivatives. References from earlier sections concerning growth of an animal, and its various tissues, are to be consulted for information, because growth of the animal and of its tissues are considered as metabolic processes. References used in this section represent metabolic changes, including utilization of oxygen by the intact test system or observations of specific tissues.

Metabolic rates were recorded as 40% below normal in treated animals, decreasing as an exponential function of time; however, in most cases, withdrawal of the drug returned the animal to near-normal values.<sup>58, 154, 287, 416, 606, 626</sup> Other such experiments indicate about 9% of loss of total thyroid hormone in the body within 24 hours, but methionine given with methylthiouracil returned the rate to normal.<sup>58, 254</sup> Dogs and guinea pigs present a species difference.<sup>191, 287</sup>

Early experiments on metabolism (dietary and chemical) established that a reduced metabolic rate also reduced the oxygen required to maintain a living system. Thiouracil and its derivatives likewise reduce utilization (or consumption) of oxygen by some 12–17%, but this is generally reversed by thyroxine.<sup>26, 63a, 66.5, 75, 417a, 604</sup> Chickens are reported to show little difference between thiouracil, thyrotropic hormone, and their rates of consumption of oxygen; whereas treated rats that were also given 2,4-dinitrophenol require increased oxygen, and their thyroids show a like increase in utilization.<sup>230, 503, 781</sup>

Hypertrophy of the thyroid and pituitary by thiouracil and derivatives should lead to inhibition in the thermo-regulating compound, *thermothyryn A*. Thiouracil-treated guinea pigs, among other animals, were found less resistant to cold through a reduced production of *thermothyryn A*; however, in a time study at low temperatures, treated rats given thyroxine showed 100% survival.<sup>85, 233, 687, 724</sup> Though thiouracil does reduce utilization of oxygen and body temperature, one set of investigators found little change in oxygen requirements when the environmental temperature was reduced.<sup>56a, 56b</sup>

Of the several hundred dietary experiments, all seem to indi-



cate a general gain of weight in animals that received thiouracil compounds. Better results are obtained with a combination of stibestrol and thiouracil.<sup>201, 314, 347, 710, 727</sup> Young pigs fed thiouracil compounds too early had retarded skeletal growth, but after proper skeletal growth was attained they thrived well when they were fed thiouracil compounds.<sup>696</sup> Less feed was required, causing better utilization of that consumed; however, the carcasses of pigs and other animals, when analyzed, gave evidence of change in composition, especially in content of nitrogen.<sup>45, 69, 93, 312, 521, 643, 673, 733</sup>

In contrast to previous reports, it appears that an increased amount of vitamin A or  $\alpha$ -carotene is needed by thiouracil-treated animals.<sup>123, 125, 137b, 171</sup> The supply of preformed thyroxine in dairy cattle appears sufficient to delay effects of thiouracil for fourteen days, after which time there is an observed increase in the titer of milk phosphatase, a lower value in lipid phosphorus, and a change in the mineral content of the animal.<sup>136, 137a, 137c, 598</sup> From a rat that had been injected with thiouracil, labeled S 35, approximately 70% of the dose was excreted in the urine in 24 hours, of which 8.3% was methylthiouracil.<sup>633</sup> Further information on metabolism may be found in the following references: <sup>12, 14, 230, 477a, 579, 589</sup>

As seen from the preceding sections, many changes are taking place in the various glands, organs, and tissues. A selected number of references are presented here toward completing the description of general effects of thiouracil on animal test systems.

Thiouracil compounds produced cellular changes usually resulting in a decreased leucocyte count; an increase in maturation time of the young forms; an increase in the number of eosinophilic granulocytes; and a reduced uptake of I 131 by erythrocytes.<sup>92, 290, 306, 398, 753</sup> One investigator reported a neutropenia in two rhesus monkeys which was resistant to pyridoxine and folic acid, and another found a transient neutropenia in mice on a pyridoxine-free diet, although thiouracil compounds were being used in both cases.<sup>35, 76</sup>

The value for ascorbic acid in plasma appeared to be stable with or without thiouracil, but the literature is confusing about its effects regarding ascorbic acid in the thyroid tissues, succinic dehydrogenase, and both the activity and content of cytochrome oxidase; however, the conversion of tyrosine to melanin by tyro-

sinase was usually inhibited by the compounds.<sup>193a, 193b, 193c, 357, 426b, 467, 497, 564b, 709</sup> The increased vascularity of the thyroid gland seemed to be related to decreased content of melanophore hormone in the pituitary.<sup>265, 411</sup> Riboflavin corrected the myelotoxic effects of thiouracil derivatives, and *in vitro* experiments demonstrated a continuing oxidation of thiouracil by myeloperoxidase, but not that of cystine.<sup>17, 671</sup>

Labeled methylthiouracil (S 35) apparently had little effect on the nucleic acid content of the test system, though thiouracil derivatives reduced the incorporation of uracil 2-C 14 into hepatomas.<sup>504, 716</sup> One research group reported a decrease in content of both ribonucleic acid (RNA) and desoxyribonucleic acid (DNA) in thyroid tissue; yet others report a substantial increase in concentration of DNA cells.<sup>608, 617, 685</sup>

Rabbits began demonstrating a decreased thrombin activity in 14 days, which stabilized about 45 days after starting studies with thiouracil, yet the phenomenon of *Arthur*—associated with production of antibodies—was drastically reduced.<sup>555, 575</sup> Chickens show two physical signs related to thiouracil; (1) a reduction in the rate of growth, the structure, and the color of feathers; (2) a decrease in the weight and production of eggs.<sup>86, 209, 391</sup> The former was reversed by discontinuing the drug.<sup>723</sup> Rats, guinea pigs, and mice showed various degrees of resistance to *Bacillus anthracis*, *Thalassin*, *Semlini Forest*, and others, depending on the nature of the treatment with thiouracil.<sup>71, 351b, 693, 697, 698</sup> Observations from experimental shock treatment—susceptibility, degree of seizure, and survival—were also apparently related to thiouracil therapy.<sup>419, 767</sup>

The rated toxicity and activity of thiouracil compounds can be found in Tables 2.1 and 2.2, and in several references: <sup>458, 660, 758</sup>. Experiments using heavy metals, chemical combinations, bacteriostatic activity, and related phenomena will be found in many references: <sup>178, 196, 206, 261, 435, 439b, 440b, 590, 610, 625a</sup>

Amphibians, tadpoles, and fish demonstrated many of the same changes as found in mammalian systems. Thiouracil (1:2000) inhibited completely the metamorphosis of *R. calmitans*; and (at 1:1000) delayed for three to six weeks the metamorphosis of *Discoglossus pictus*.<sup>194a, 194b, 337</sup> Lactoflavin restored the growth of certain tadpoles, but the *Rana sylvatica* in its tail-bud stage showed marked blanching of pigment, which was overcome when

TABLE 2.1  
*Antithyroid Compounds*

<i>Chemical Name</i>	<i>Effectiveness</i>	<i>Reference</i>
Thiouracil	1	601, 750
6-Methylthiouracil	>1	353, 750, 762
5-Methylthiouracil	<1	179, 750
Benzylthiouracil	<1	457, 601, 750
6-Phenylthiouracil	<1	750
Cyclopropylthiouracil	>1	332b, 754
Isobutylthiouracil	>1	754
Butylthiouracil	>1	754
Amylthiouracil	>1	754
5-Ethylthiouracil	>1	754
6-Propylthiouracil	>1	58, 457, 601, 750, 762
4-Methyl-5-butylthiouracil	-	517
4-Methyl-5-benzylthiouracil	-	517
6-Methyl-4-thiouracil	0	353
6-Methyl-5-ethyl-2-thiouracil	>1	353
Tetramethylenethiouracil	>1	40, 59
Diethylthiouracil	>1	40
Diisopropylthiouracil	>1	40
5-Iodo-2-thiouracil	-	755
6-Methyl-5-iodo-2-thiouracil	-	755

TABLE 2.2  
*Antithiouracil Compounds*

<i>Chemical Name</i>	<i>Reference</i>
Iodine or iodide ion	108, 173, 319, 396, 461, 523 409, 455, 714
BAL	254
Copper	176b
Mercury	176b
Potassium thiocyanate	305, 603, 629, 714, 715b
Methionine	254
Arsenic oxide	176a
Cadmium	176a
Zinc	176a
Iron	176a

the drug was removed.<sup>357a, 452, 487, 611, 613</sup> Thiouracil or its derivatives are reported as having changed the cellular elements in a frog; decreased both the metabolic rate and the consumption of

oxygen in fish and tadpoles; and increased the rate of uptake of I <sup>131</sup> in tadpoles.<sup>435, 448, 526, 554</sup>

Man responds to disease and treatment in much the same manner as animals. His unique position is the physical ability to express this response to observers and recording instruments, thus enabling the medical and para-medical discipline to formulate more effective therapy and treatment. The medical literature on thiouracil and its derivatives, in relation to conditions of the thyroid, and general bodily health, offers considerable duplication about the original use of the drug for hyperthyroidism. This is important, however, when considering side effects, or changes in the condition of a patient following treatment with thiouracil. Several pertinent references with both general and specific information of this point are:<sup>286, 428, 543, 572, 699, 708, 753</sup>

The diagnosis of hyperthyroidism was once confined to external signs such as changes in weight, development of goiter, increased nervous tension, exophthalmos, and elevated rate of basal metabolism (BMR), and the treatment of it was as varied as the opinions held about the condition. Surgical procedures offered hope of restoring a patient to a more normal life, but they were considered dangerous.

One of the earlier indices of the effectiveness of thiouracil in hyperthyroidism was the combined decrease in BMR and increase in blood cholesterol; however, in recent years, this has largely been superseded by chemical determinations of protein-bound iodine (PBI) in the patient's serum; the rate of uptake of I <sup>131</sup> by the thyroid; and the amount of I <sup>131</sup> in the blood (both bound to proteins and unbound), and in the urine.<sup>74, 84, 113, 170, 600, 601, 769</sup> Thiouracil has been used as a diagnostic means of distinguishing patients with normal thyroid from those in which a hyper- or hypothyroid condition may be suspected.<sup>170, 638</sup>

Histological changes suggestive of a more normal state of activity have been seen in thiouracil-treated hyperthyroid conditions, with similar changes in the anterior hypophysis and adrenal cortex; however, propylthiouracil showed signs of inhibiting the iodine-accumulating ability of the thyroid gland.<sup>57, 202, 344, 602</sup> There is a report of no histological improvement of thyroid tissue by thiouracil.<sup>70</sup>

Changes in the blood, such as leucopenia, agranulocytosis, granulocytopenia, hepatocellular jaundice, and thrombopenic pur-

pura, were the major side effects found as a result of treatment with thiouracil or its derivatives. There are conflicting reports on these conditions, but all the investigators agree that patients should be followed closely because their tolerance to thiouracil compounds and supporting medication could result in a secondary complication more difficult to control.

An increased leucocyte count (Wbc) was usually found in normal subjects on thiouracil, but treated hyperthyroid patients had lower Wbc counts, with lower erythrocyte counts (Rbc) and a reduced Wbc/Rbc ratio in bone medulla; however, both the Wbc and Rbc had increased time of maturation.<sup>295, 446, 470, 558, 596</sup> The granulocytotic effects of thiouracil drugs seemed to be overcome by administering pyridoxine; or simply by withdrawing thiouracil.<sup>249, 692</sup> Leukemia patients on thiouracil therapy exhibited a marked decrease in Wbc's but an increased value for blood uric acid; other cases had no demonstrable effects in the myeloid dysfunction of bone marrow.<sup>307, 558</sup>

During the course of treating thyrotoxicosis with thiouracil drugs, several biochemical changes that were seen were suggestive of a toxic action on the metabolism and functioning of the liver; decreased rate of disappearance of glucose from blood; elevated hyperglycemic coefficient; attainment of near-normal balance of these changes with insulin; and reduced synthesis of hippuric acid.<sup>592</sup> Improvement in the liver was indicated by an increased prothrombin time, but it was suggested that vitamin K be given with the drug to restore prothrombin activity to normal.<sup>124, 429</sup>

Other observations covering specialized tissues are as follows: Both the lipid content and oxygen consumption of patients with lupus erythematosus were little affected by propylthiouracil;<sup>451</sup> normally increased cholinesterase activity of hyperthyroid patients was reduced by thiouracil medication;<sup>18, 19</sup> there was no consistent evidence of any influence by thiouracil on the magnesium levels in normal subjects. Methylthiouracil seemed to stabilize the value of blood iron in hyperthyroid patients; it augmented the penetration of ethanol into tissue but not into blood;<sup>91, 134, 545</sup> and thiouracil causes changes (increases and decreases) in the metabolism and distribution of sulfur.<sup>752</sup>

Blood and urine from treated hyperthyroid patients, when analyzed for calcium, sodium, phosphorus, chloride, nitrogen,

creatinine, and creatinine, indicated changes corresponding to an improved physiological state, similar to that seen in a subtotal thyroidectomy.<sup>65, 663, 749</sup> The normal conversion of tyrosine to melanin by tryosinase was diverted to produce homogentisic acid found in the blackish urine of melanosarcomic patients.<sup>661</sup> Medication with thiouracil compounds restored normal color to the urine (which becomes blackish if the drug is withdrawn), thus reducing the amount of this acid; this failed in certain alkaptonuric patients.<sup>703, 743, 744</sup>

A reduced output of 17-keto steroids in the urine, found in patients with Basedow's syndrome, was increased by thiouracil drugs, and riboflavin administered simultaneously with the drug reduced the increased pulse rate and blood pressure in some of these patients.<sup>236, 627, 653</sup> Thiouracil also lowered the systolic-diastolic blood pressure and altered the "T" waves (electrocardiogram) of ten male psychotic patients; propylthiouracil, however, demonstrated little change in BMR or in altering the menstrual cycle of euthyroid females.<sup>593, 684</sup>

About 50% of a dose of thiouracil (oral ingestion or intravenous injection) was lost or destroyed in the gastro-intestinal tract and body tissues.<sup>752</sup> Table 2.3 compares the potencies of

TABLE 2.3

*Thyroid I 131 Index of Thiouracil Compounds*

<i>Compound</i>	<i>Thyroid I 131 Index</i>
Thiouracil	1.0
6-Methylthiouracil	2.0
6-Ethylthiouracil	1.0
6-Cyclopropylthiouracil	1.0
6-Isopropylthiouracil	1.0
6-Propylthiouracil	0.75
6-Tertbutylthiouracil	0.25
6-Butylthiouracil	0.75
6-Hexylthiouracil	0.5
6-Benzylthiouracil	0.75
6-Aminothiouracil	0.1

several thiouracil derivatives to thiouracil, using I 131 techniques.<sup>675</sup> The following references should be consulted for further

information on thiouracil compounds, their toxicity, and their effects: 80, 130, 131, 237, 292, 294, 317, 410, 450, 535, 725

Thiouracil and its derivatives inhibited or retarded the growth of certain bacteria, viruses, and plants (see Table 2.4) by being chemically incorporated into the structure of the cells, in much the same way as the synthesis of nucleic acid occurs in the cells of various tissues.<sup>320</sup>

TABLE 2.4

*Inhibiting Effect of Thiouracil on Growth of  
Certain Bacteria, Virus, and Plants*

<i>Bacteria</i>	<i>Virus</i>	<i>Plants</i>
<i>Bacillus megatherium</i>	Influenza	<i>Aspargillus terrus</i>
<i>Lactobacillus casei</i>	Psittacosis	<i>Byrophyllum tribiflorum</i> <sup>325</sup>
<i>Escherichia coli</i>	Tobacco mosaic	<i>Tradescandia</i> <sup>325</sup>
<i>Streptococcus faecalis</i>		"Khapli" flower <sup>630</sup>
<i>Streptococcus viridans</i> <sup>522</sup>		

The strain 15T<sup>-</sup> of *E. coli* demonstrated two changes: (1) A reduction of glucose and oxidation of furanose-1,6-diphosphate; and (2) the appearance of 6-methylaminopurine as a part of its DNA.<sup>157, 216, 217</sup> The K-12 strain apparently synthesized thio-uridylides from thiouracil and ribose-5'-phosphate; whereas the  $\beta$ -galactosidase activity of strain ML 37 and ML 308 was strongly inhibited by thiouracil.<sup>22, 304</sup>

In order of decreasing activity, thiouracil, 5-iodo-thiouracil, and 5-iodo-2-benzylthiouracil inhibited the growth of *Streptococcus faecalis*,<sup>199, 591</sup> yet, the presence of folic acid or thymine did not seem to reduce the inhibiting effects of 2,4-dithiouracil, 2-thio-5,6-diaminouracil, or 2,4-dithiothymine.<sup>205, 471</sup> *Coccynebacterium diphtheria* produced both a virulent and an avirulent phase—each interchangeable—as a result of exposure to thiouracil compounds, and a growth medium inoculated with *Streptomyces sayamaensis* had an increase of tetracycline.<sup>37, 313</sup>

Several thiouracil compounds were found effective against the growth of *Lactobacillus casei*.<sup>764</sup> Thiouracil demonstrated two effects of *Bacillus megatherium*: 1) From thiouracil-S 35, 20% S 35 was found incorporated into the RNA in the bacilli; 2) from experiments with unlabeled thiouracil, the synthesis of the RNA of the specific bacteriophage in the bacilli was inhibited

more than that of the RNA in the cells of the bacilli.<sup>303, 352c</sup>

Thiouracil also exhibited the incorporation of guanine-C 14 and P 32 into the RNA of the influenza virus. Thiouracil did not retard the growth of *psittacosis* virus (6 BC strain); methylthiouracil was without visible effects on it.<sup>21, 534</sup> It was noted that uracil usually countered these effects and revived the growth of the organism.

Thiouracil, 6-methylthiouracil, and 6-propylthiouracil not only inhibited the growth of tobacco mosaic virus (TMV), but thiouracil also appeared to affect its carbohydrate metabolism, and S 35 (from thiouracil-S 35) was found in the structure of the RNA of the virus.<sup>167, 187, 352a, 352b, 474, 506, 547</sup>

Thiouracil was effective against the stone fruit virus of the plum and the cucumber mosaic virus, but was only moderately so on TMV of tomato seedlings.<sup>407, 587</sup>

Methylthiouracil inhibited the germination of *Cress* seed;<sup>707</sup> and thiouracil, when sprayed on olive trees and grape vines, reduced their synthesis of RNA and protein, accelerated sub-cotyledonar growth while decreasing supercotyledonar growth of certain lupine plants, and curtailed the production of *eodin*, an antibiotic from *Aspergillus terrus*.<sup>266, 404, 498</sup> Information concerning the effect of thiouracil on other bacteria, viruses, and plants will be found in the following references:<sup>97, 198, 325, 567, 630, 694, 702, 718</sup>

### Physical Properties of Some Thiopyrimidines and Derivatives

Some hundreds of thiopyrimidine derivatives are given in the following lists without any claim for completeness. The chief object is to give references so that the preparation of each compound may be traced. Where the same compound has been reported by several authors, the melting points are frequently divergent. There has been a greater urge to get a compound for some particular use than there has been to purify and characterize it properly. There are even cases of mistake identity. It is possible that different methods of preparation may have given the tautomers of a compound in different proportions.

As was stated in the introduction to this chapter, almost all thiopyrimidines are tautomeric and, as such, may have two, or even more, systematic names. Thus, thiouracil is 2-mercapto-4-



hydroxy-pyrimidine or 2-thio-4-keto-tetrahydropyrimidine. In consequence there is great confusion in the nomenclature. *Beilstein* and *Chemical Abstracts* do not always agree on the name of a compound and the chemist that made it may call it something different.

The earliest study on the ultraviolet absorption spectra of thiopyrimidines was concerned with 2-thio-, 2,4-dithio-, and 4-thiouracils at pH values 1, 7, and 11.<sup>228</sup> A notable bathochromic effect was observed when furyl and furylmethyl groups were introduced into the 6-position of 2-thiouracil. Ultraviolet spectra have been determined for a number of 6-substituted-2-thiouracils at pH 1.03, 2.86, 5.6, 10.2, and 12.9.<sup>29a</sup> The bathochromic shift varies according to the position of the substituent in the pyrimidine ring. The order in which the substituents are arranged depends on whether they are in the 2- or the 4-position.<sup>94c</sup>

The effect of chemical structure and varying pH on the position of the maximum has been investigated for 2-mercapto-4,6-dihydroxy-5-ethyl- and 2-mercapto-4,6-diaminopyrimidine. The shifting of the maximum with pH depends not so much on the actual symmetry of the molecule as on the possibility of formation of an anion or cation.<sup>680</sup> Ultraviolet spectra have been reported for 2-mercapto-4,5-diaminopyrimidine at pH 1.0, 6.5, and 12.4;<sup>546</sup> and for some 4,5,6-triamino-2-mercaptopyrimidines.<sup>83</sup>

Infrared values have been obtained for 2-methylmercaptopyrimidines<sup>657</sup> and for a number of 4,6-diamino-2-mercapto- and 2-methylmercaptopyrimidines.<sup>114, 115</sup>

The dipole moments of 2-thiouracil and of some derivatives of 4-thiouracil, 2,4-dithiouracil, and 2-methylmercapto-4-thiouracil have been determined.<sup>642</sup>

## 2-MERCAPTOPYRIMIDINE AND DERIVATIVES

Unsubstituted, m. 230° (dec.).<sup>94a, 463, 657</sup>

### *Monosubstituted 2-Mercaptopyrimidines*

4-Ethoxy, b<sub>11</sub> 123–4°; n. 1.5405.<sup>146</sup>

4-Amino(Thiocytosine), m. 285–90°, <sup>117a, 322</sup> 278° (dec.).<sup>622</sup>

4-Methylamino, m. 237°. <sup>117a, 323b, 622</sup>

4-[Diphenylmethylamino], m. 250–60° (dec.). <sup>117a, 622</sup>

4-[2-(2-Diethylamino)ethylamino], m. 115°. <sup>117a, 323b, 622</sup>

4-(2-Hydroxyethylamino), m. 226–8°. <sup>117a, 323b, 622</sup>

- 4-[2-(4-Morpholinyl)ethylamino], m. 243° (dec.).<sup>117a, 622</sup>  
 4-Methylpropylamine, m. 195°.<sup>117a</sup>  
 4-Amylamino, m. 218°.<sup>117a, 323b, 622</sup>  
 4-Tetradecylamino, m. 149°.<sup>117a, 323b, 622</sup>  
 4-Anilino, m. 285° (dec.).<sup>117a, 323b, 622</sup>  
 4-(*p*-Chloranilino), m. 299° (dec.).<sup>117a, 323b, 622</sup>  
 4-(*p*-Methoxyanilino), m. 264.5°.<sup>622</sup>  
 4-(*N*-Methylanilino), m. 250–3°.<sup>117a, 622</sup>  
 4-Benzylamino, m. 249°.<sup>117a, 323b</sup>  
 4-Phenyl, m. > 180° (dec.).<sup>132</sup>  
 4-(1-Piperidyl), m. 228°.<sup>117a, 622</sup>  
 4-(4-Methyl-1-piperazinyl), m. 257°.<sup>117a, 622</sup>  
 4-(4-Morpholinyl), m. 248–50°.<sup>117a, 622</sup>  
 5-Ethoxy, m. 193°.<sup>377a</sup>

### Disubstituted

- 4-Hydroxy-5-carboxy, m. 289° dec.; NH<sub>4</sub> salt, m. 308–10° (dec.).<sup>466b</sup>  
 4-Ethoxy-5-carbethoxy, b<sub>8</sub> 175°; n<sub>D</sub> 24.5/D 1.5420.<sup>146</sup>  
     -5-methyl, b<sub>12</sub> 135–6°; n<sub>D</sub> 24/D 1.5365.<sup>146</sup>  
     -5-bromo, b<sub>8</sub> 140°; n<sub>D</sub> 22.5/D 1.5787.<sup>146</sup>  
 4,5-Diamino, m. 250° (dec.).<sup>227b</sup>  
 4-Amino-5-methyl, m. 274°.<sup>117a, 322, 622</sup>  
     -5-ethyl, m. 274° (dec.).<sup>323d</sup>  
     -5-carbethoxy (5-carbethoxy-2-thiocytosine), m. 260–5°.<sup>360</sup>  
     -5-(3,4-dichlorophenyl), decomp. 270° m. 298–302°.<sup>117b</sup>  
     -5-phenoxy, m. 270° (dec.).<sup>117b, 323d</sup>  
     -5-(3,4-dimethylphenoxy), m. 270–4° (dec.).<sup>323d</sup>  
     -5-(3-Me-4-chlorophenoxy), m. 258–63° (dec.).<sup>323d</sup>  
     -5-(*p*-ClC<sub>6</sub>H<sub>4</sub>O), m. 255–9° (dec.).<sup>323d</sup>  
     -5-(2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O), m. 260–4° (dec.).<sup>323d</sup>  
     -5-(2,4-Cl(Me<sub>3</sub>C)C<sub>6</sub>H<sub>3</sub>O), m. 276–80° (dec.).<sup>323d</sup>  
     -5-benzyl.<sup>323d</sup>  
     -5-(*p*-chlorobenzyl), m. 235° (dec.) again at 243°.<sup>323d</sup>  
 4-Methylamino-5-amyl, m. 198°.<sup>323b</sup>  
     -5-benzyl, m. 248°.<sup>117b, 622</sup>  
 4-Amylamino-5-methyl, m. 198°.<sup>117b, 323b, 622</sup>  
 4-Anilino-5-methyl, m. 232–4°.<sup>117b, 622</sup>  
 4,6-Dimethyl, m. 198°,<sup>628</sup> 208–10°,<sup>94a</sup> 210°; 29a, 30, 235 HCl, m. 260° (dec.).<sup>94a</sup>

- 4-Methyl-6-amino, m. 280°. <sup>267, 622</sup>  
 -6-amylamino, m. 221° (dec.). <sup>117a, 323b, 622</sup>  
 -6-phenyl, m. 200°. <sup>726</sup>  
 -6-anilino, m. 230° (dec.). <sup>117a, 323b, 622</sup>  
 -6-(1-piperidyl), m. 203-5°. <sup>117a, 622</sup>  
 -6-(EtO)<sub>2</sub>P(S)O, b<sub>0.3</sub> 132-3°; <sup>146, 505</sup> d 20/4 1.1577; <sup>505</sup>  
 n 20/D 1.5364. <sup>146, 505</sup>  
 4-Amyl-6-anilino, m. 228°. <sup>323b</sup>  
 4-Methoxy-6-benzyl, m. 66°. <sup>439c</sup>  
 4-(3-Methoxypropylamino)-6-*p*-ClC<sub>6</sub>H<sub>4</sub>, m. 243-5°. <sup>117a</sup>  
 4-Amylamino-6-phenyl, m. 228°. <sup>117a, 323b, 622</sup>  
 4-Phenyl-6-(*p*-methoxyanilino), m. 265°. <sup>117a, 323b</sup>

### Trisubstituted

- 4,5-Dimethyl-6-amino, m. 300°. <sup>639</sup>  
 4-Methyl-5-nitro-6-amino, m. 270° (dec.), <sup>585b</sup> 240-50° (dec.). <sup>585a</sup>  
 4-Chloro-5-bromo-6-amino, m. 165°. <sup>335</sup>  
 4,6-Diamino-5-ethyl, m. 292° (dec.). <sup>240b</sup>  
 -5-bromo, m. 192°. <sup>335</sup>  
 -5-formamido. <sup>703</sup>  
 4,5,6-Triamino. <sup>703</sup>  
 4-Amino-5-*p*-chlorophenyl-6-ethyl, black at 230°, m. 326°  
 (dec.). <sup>324</sup>  
 4-Dimethylamino-5-nitro-6-methyl, m. 224°. <sup>619b</sup>  
 4-Benzylmethylamino-5-nitro-6-methyl, m. 198°. <sup>619b</sup>

### 2-METHYLMERCAPTOPYRIMIDINE AND DERIVATIVES

- Unsubstituted, b<sub>14</sub> 99-100°; <sup>377a, 494a</sup> b<sub>16</sub> 102-3°; <sup>494b</sup> b<sub>28</sub> 109°;  
 n 14/D 1.5880; <sup>94c</sup> n 20/D 1.5856; HCl, m. 147°; <sup>377a</sup> 142.4°; <sup>311</sup>  
 Picrate, m. 89-91°; <sup>494b</sup> HBr, m. 188° (dec.); Monohydroxy-  
 methyle, m. 146°. <sup>377a</sup>

### Monosubstituted

- 4-Methyl, b<sub>1</sub> 78-80°; <sup>494a</sup> Picrate, m. 108-10°. <sup>494a, 494b</sup>  
 4-Chloro, b<sub>36</sub> 139-40°; <sup>176b</sup> 122°. <sup>494a</sup>  
 4-Amino, m. 126°; <sup>735</sup> 1-Methiodide, m. 227° (dec.). <sup>9</sup>  
 4-Phenyl, m. 87.5°. <sup>494b</sup>  
 4-(4-Diethylamino-1-methylbutylamino), b<sub>0.9</sub> 176-8°. <sup>180</sup>  
 4-TriAc-O-xylosidamino, m. 191°. <sup>334</sup>  
 5-Bromo, m. 65°; HBr, m. 206°. <sup>377b</sup>  
 5-Nitro, m. 83°. <sup>94a</sup>

*Disubstituted*

- 4-Methyl-5-amino, m. 142.5°. <sup>46b</sup>  
 -5-nitro, m. 78°. <sup>619b</sup>  
 -5-(*p*-O<sub>2</sub>N·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>NH), m. 139°. <sup>46b</sup>  
 -5-(*p*-H<sub>2</sub>N·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·NH), m. 241°. <sup>46b</sup>  
 4-Hydroxy-5-carboxy, m. 235°; Et ester, m. 134-6°. <sup>466b</sup>  
 4-Chloro-5-bromo, m. 44°. <sup>377b</sup>  
 4-Chloro-5-ethoxy, m. 75°. <sup>368</sup>  
 4-Amino-5-methyl, m. 131°. <sup>109</sup>  
 4,6-Dimethyl, m. 24°; <sup>302, 736</sup> b<sub>33</sub> 144°, b<sub>14</sub> 123-5°, <sup>736</sup> b<sub>17</sub> 120-2°. <sup>29a</sup>  
 4-Methyl-6-methoxy, b<sub>12</sub> 125-30°. <sup>465</sup>  
 -6-ethoxy, m. 41°; Picrate, m. 84°. <sup>585c</sup>  
 -6-allyloxy, b<sub>17</sub> 160-4°. <sup>370</sup>  
 -6-chloro, m. 40°, <sup>741a</sup> 38°, <sup>465, 494a</sup> 20-3°; <sup>109</sup> b<sub>2</sub> 97-9°, <sup>494a</sup> b<sub>15</sub> 132°, <sup>109</sup> b<sub>32-5</sub> 147°. <sup>741</sup>  
 -6-amino, m. 131°, <sup>584</sup> 137°, <sup>46b</sup> 133.5-5°; <sup>340</sup> 1-Methiodide, m. 261°. <sup>9</sup>  
 -6-methylamino, m. 112-3°. <sup>583</sup>  
 -6-butylamino, 1-Methiodide, m. 164°. <sup>6, 7</sup>  
 -6-(2-diethylaminoethylamino), b<sub>1.2</sub> 150-1.5°; Dipicrate, m. 155-7°. <sup>180</sup>  
 -6-(3-diethylaminopropylamino), b<sub>1</sub> 168-70°; Dipicrate, m. 125-7°. <sup>180</sup>  
 -6-(6-bromo-2-naphthylamino), m. 171°. <sup>183</sup>  
 -6-phenyl, b<sub>1</sub> 154-60°. <sup>109</sup>  
 -6-anilino, m. 114°; HCl, m. 225°. <sup>585c</sup>  
 -6-(*p*-toluidino), m. 163°. <sup>183</sup>  
 -6-(*p*-methoxyanilino), m. 114°. <sup>183</sup>  
 -6-(*p*-chloroanilino), m. 172°. <sup>181a, 183</sup>  
 -6-(1-piperidyl), Acid oxalate, m. 149°. <sup>585c</sup>  
 -6-(*p*-O<sub>2</sub>N·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·NH), m. 186°. <sup>46b</sup>  
 -6-(*p*-acetamidophenylsulfonyl), m. 207°. <sup>585c</sup>  
 -6-(*p*-H<sub>2</sub>N·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·NH), m. 214.5°. <sup>46b</sup>  
 -6-(EtO)<sub>2</sub>(O)PO, b<sub>0.05</sub> 152-4°. <sup>271b</sup>  
 4-Methoxy-6-amino, m. 256°; <sup>374b</sup> Ac, m. 165°. <sup>576</sup>  
 -6-(2-furyl), m. 151°. <sup>28c</sup>  
 4,6-Dichloro, m. 42°; b<sub>14</sub> 135-6°. <sup>736</sup>  
 4-Chloro-6-amino, m. 131°, <sup>51</sup> 132°, <sup>374a, 374b</sup> 127°, <sup>52</sup> 128°. <sup>736</sup>  
 -6-methylamino, m. 131°. <sup>6, 7</sup>

- 4,6-Diamino, m.  $185^{\circ}$ ; <sup>374a, 374b</sup>  $186^{\circ}$ ; <sup>50b, 354d</sup> Picrate, m.  $212^{\circ}$  (dec.); 6-Ac, m.  $226^{\circ}$ ; HCl, 1 mol.  $H_2O$  m.  $214^{\circ}$ .<sup>50b</sup>
- 4-Amino-6-methylamino, m.  $144^{\circ}$ .<sup>49</sup>
- 6-dimethylamino, m.  $162-4^{\circ}$ ; HCl, m.  $282^{\circ}$ .<sup>52</sup>
  - 6-diethylamino, Picrate, m.  $212^{\circ}$ .<sup>53</sup>
  - 6-benzylbutylamino, HCl, m.  $150^{\circ}$ .<sup>53</sup>
  - 6-anilino, m.  $121^{\circ}$ ; <sup>374a</sup>  $124^{\circ}$ .<sup>374b</sup>
  - 6-N-methylanilino, m.  $123-5^{\circ}$ ; HCl, m.  $254^{\circ}$  (dec.).<sup>53</sup>
  - 6-piperidino, m.  $151-3^{\circ}$ .<sup>53</sup>
- 4,6-bis-(Methylamino), m.  $152-3^{\circ}$ ; 1-Methiodide, m.  $223^{\circ}$ .<sup>6, 7</sup>
- 4-Dimethylamino-6-ethylamino, m.  $127^{\circ}$ .<sup>52</sup>
- 4-D-Xylosidamino-6-amino, m.  $190-2^{\circ}$  (dec.);  $[\alpha]$   $17.5/D$   $-20^{\circ}$ ; <sup>334</sup> 6-NHAc, I, m.  $95-100^{\circ}$  (from  $H_2O$ ),  $192-3^{\circ}$  (from EtOH)  $[\alpha]$   $20/D + 23^{\circ}$ ; <sup>50b</sup> II, m.  $175-80^{\circ}$ .<sup>334</sup>
- 4-(Triacetyl-D-Xylosidamino)-6-NHAc, (I), m.  $226^{\circ}$  (dec.);  $[\alpha]$   $18/D + 57^{\circ}$ ; <sup>50b</sup> (II), m.  $218^{\circ}$   $[\alpha]$   $18/D + 48.4^{\circ}$ .<sup>334</sup>
- 4-D-Mannosidamino-6-amino, 1.5 mols  $H_2O$ , m.  $214^{\circ}$  (dec.); Ac, m.  $242-3^{\circ}$  (dec.);  $[\alpha]$   $20/D - 55^{\circ}$ .<sup>50b</sup>
- 4-Tetra-acetyl-D-mannosidamino-6-NHAc, 3 mols  $H_2O$ , m.  $140-50^{\circ}$ ;  $[\alpha]$   $20/D - 100^{\circ}$ .<sup>50b</sup>
- 4-D-Xylosidamino)-6-NHAc, I, m.  $95-100^{\circ}$  (from  $H_2O$ ) m.  $193^{\circ}$  (from EtOH);  $[\alpha]$   $20/D + 23^{\circ}$ .<sup>50b</sup>

### Trisubstituted

- 4-Methyl-5-acetyl-6-benzylmethylamino, m.  $102^{\circ}$ .<sup>619b</sup>
- 5-bromo-6-chloro, m.  $72-3^{\circ}$ .<sup>181b</sup>
  - 6-(p-chloroanilino), m.  $117^{\circ}$ .<sup>181b</sup>
  - 5-nitro-6-benzylmethylamino, m.  $90^{\circ}$ .<sup>619b</sup>
- 4-Ethyl-5-(p-chlorophenyl)-6-amino, m.  $156^{\circ}$ .<sup>324</sup>
- 4-Ethoxy-5-methyl-6-chloro, m.  $85^{\circ}$ .<sup>738</sup>
- 4,6-Dichloro-5-methyl, m.  $64^{\circ}$ ; b.  $135-4^{\circ}$ .<sup>738</sup>
- 4-Chloro-5,6-dimethyl, m.  $36^{\circ}$ .<sup>177, 340, 738</sup>
- 5-methyl-6-methylamino, m.  $157^{\circ}$ .<sup>738</sup>
  - 6-amino, m.  $165^{\circ}$ ; HCl, m.  $208^{\circ}$  (dec.).<sup>374b</sup>
- 4-Amino-5,6-dimethyl, m.  $159^{\circ}$ .<sup>177, 340</sup>
- 5-bromo-6-amino, m.  $192^{\circ}$ .<sup>374b</sup>
  - 6-[4-bromoanilino], m.  $202^{\circ}$ .<sup>374b</sup>
  - 5-NO-6-dimethylamino, m.  $220^{\circ}$  (dec.).<sup>52</sup>
  - 6-diethylamino, m.  $134^{\circ}$  (dec.).<sup>53</sup>
  - 6-benzylbutylamino, HCl, m.  $119^{\circ}$ .<sup>53</sup>

- 6-N-methylanilino, HCl, m. 197.5°. <sup>53</sup>  
 -6-piperidino, m. 170° (dec.). <sup>53</sup>  
 4,5,6-Triamino, m. 182°; <sup>49</sup> 5-formamido, m. 254° again at 280-90°; <sup>334</sup> 5-thioformamido, m. 235° (dec.). <sup>49, 334</sup>  
 4,5-Diamino-6-dimethylamino, m. 155°; 5-formamido, m. 226° (dec.) m. again at 280°. <sup>52</sup>  
 4-Amino-5-formamido-6-diethylamino, m. 155°. <sup>53</sup>  
     -6-N-methylanilino, HCl m. 213°. <sup>53</sup>  
     -6-piperidino, m. 185-7°. <sup>20b, 53</sup>  
     -6-benzylbutylamino, HCl, m. 151°. <sup>20b, 53</sup>  
     -5-thioformamido-6-methylamino, m. 186°. <sup>49</sup>  
     -5-methylamino-6-dimethylamino, m. 167°. <sup>52</sup>  
     -5-tosylamino-6-dimethylamino, m. 209°; HCl, m. 266° (dec.). <sup>52</sup>  
     -5-N-methyltosylamino-6-dimethylamino, m. 233°. <sup>52</sup>  
 4-Dimethylamino-5-NO-6-ethylamino, m. 120°. <sup>52</sup>  
 4-Benzylmethylamino-5-nitro-6-methyl, m. 90°. <sup>619b</sup>  
 4-(D-Xylosidamino)-5-NO-6-amino I, m. 237°; II, m. 197°; triAc, m. 193°. <sup>334</sup>  
     -5,6-diamino,-5-formamido, 1 mol H<sub>2</sub>O, m. 232°; triAc, m. 191°; -5-thioformamido, 1 mol H<sub>2</sub>O, m. 208° (dec.); triAc, m. 209°. <sup>334</sup>  
 4-D-Mannosidamino-5-NO-6-amino, m. 231° (dec.). <sup>453</sup>  
     -5,6-diamino,-5-formamido, m. 232° (dec.);  
     -5-thioformamido, m. 217-9° (dec.). <sup>453</sup>  
 4-(Tetraacetyl-D-glucocylamino)-5-NO-6-amino, m. 154°. <sup>255</sup>  
     -5,6-diamino, m. 214°; 5-chloro-acetamido, m. 139°; HCl, m. 164°. <sup>294</sup>

## 2-ETHYLMERCAPTOPYRIMIDINE AND DERIVATIVES

Unsubstituted,  $b_{20}$  115°;  $n_{20/D}$  1.5673; HCl, m. 99°; HBr, m. 141°; 1-methiodide, m. 135°. <sup>377a</sup>

### *Monosubstituted*

- 4-Methyl,  $b_{18-19}$  123-4°; HCl, m. 142°. <sup>377a</sup>  
 4-Ethoxy,  $b_{18-19}$  137-8°. <sup>738b</sup>  
 4-Chloro, m. 150°; <sup>129, 738a</sup>  $b_{24}$  135°. <sup>738b</sup>  
 4-Amino, m. 86°. <sup>735, 738a</sup>

- 4-Methylamino, m.  $58^{\circ}$ ,<sup>129</sup>  $55^{\circ}$ .<sup>354b</sup>  
4-Ethylamino,  $b_{11}$   $195.5^{\circ}$ .<sup>356a</sup>  
4-Thiocyano, m.  $82^{\circ}$ .<sup>388</sup>  
4-Isothiocyano,  $b_{45-50}$   $200-5^{\circ}$ .<sup>735</sup>  
4-NH<sub>2</sub>·CS·NH, m.  $214^{\circ}$ .<sup>735</sup>  
4-EtO·CS·NH, m.  $93^{\circ}$ .<sup>735</sup>  
4-Anilino, m.  $68^{\circ}$ ; HCl, m.  $198^{\circ}$ ,<sup>735</sup>  $197^{\circ}$  (dec.).<sup>622</sup>  
4-(3-Nitroanilino), m.  $175^{\circ}$ ; HCl, m.  $140-55^{\circ}$ .<sup>375</sup>  
4-(Toluidino), *o*-, m.  $87^{\circ}$ ; HCl, m.  $230-2^{\circ}$ ; *p*-, m.  $198-207^{\circ}$ ; HCl, m.  $201^{\circ}$ .<sup>375</sup>  
4-(PhNH·CS·NH), m.  $205^{\circ}$ .<sup>735</sup>  
5-Ethoxy, m.  $32^{\circ}$ ; HCl, m.  $121^{\circ}$ .<sup>377a</sup>  
5-Bromo, m.  $43-5^{\circ}$ ; HBr, m.  $180^{\circ}$ .<sup>377b</sup>

*Disubstituted*

- 4-Ethoxymethyl-5-ethoxy, m.  $167^{\circ}$ .<sup>362</sup>  
4-Methoxy-5-methyl,  $b_4$   $104-5^{\circ}$ .<sup>144c</sup>  
4-Chloro-5-methyl,  $b_{15-18}$   $145-7^{\circ}$ ,<sup>308</sup>  $b_{25}$   $157-9^{\circ}$ .<sup>738b</sup>  
-5-carboxymethyl, m.  $132^{\circ}$ ; <sup>387</sup> Et ester, b.  $172-4^{\circ}$ .<sup>148</sup>  
-5-ethyl,  $b_{22}$   $160-3^{\circ}$ .<sup>149b</sup>  
-5-ethoxy, m.  $46^{\circ}$ ;  $b_{25}$   $185^{\circ}$ .<sup>378b</sup>  
-5-bromo, m.  $27^{\circ}$  (cir),<sup>738a, 738b, 738c</sup>  $b_{24-5}$   $168^{\circ}$ ,  $b_{36}$   $179-80^{\circ}$ .<sup>735</sup>  
-5-iodo, m.  $69^{\circ}$ .<sup>735</sup>  
-5-fluoro.<sup>222</sup>  
-5-methylamino, m.  $112^{\circ}$ ; HCl, m.  $182-4^{\circ}$  (dec.).<sup>211b</sup>  
-5-cyano, m.  $36^{\circ}$ ;  $b_{13}$   $163^{\circ}$ .<sup>211b</sup>  
-5-phenyl, b.  $231-2^{\circ}$ .<sup>149a</sup>  
4,5-Diethoxy, m.  $129-31^{\circ}$  (dec.).<sup>372b</sup>  
4-Amino-5-methyl, m.  $97^{\circ}$ .<sup>738b</sup>  
-5-hydroxymethyl, m.  $170^{\circ}$ ; HCl, m.  $162^{\circ}$ .<sup>211b</sup>  
-5-chloromethyl, HCl, m.  $202-4^{\circ}$ .<sup>211b</sup>  
-5-bromomethyl, HBr, m.  $283-5^{\circ}$  (dec.).<sup>211b</sup>  
-5-ethyl, m.  $74-6^{\circ}$ .<sup>380</sup>  
-5-ethoxy, m.  $105^{\circ}$ .<sup>378b</sup>  
-5-bromo, m.  $124^{\circ}$ .<sup>374a, 738a, 738b, 738c</sup>  
-5-iodo, m.  $127^{\circ}$ .<sup>374a</sup>  
-5-fluoro, m.  $94^{\circ}$ .<sup>222, 327</sup>  
-5-carboxy, m.  $230^{\circ}$ ; <sup>737a</sup> Et ester, m.  $102^{\circ}$ .<sup>358a</sup>  
-5-methylamino, m.  $148^{\circ}$ .<sup>211b</sup>

- 5-cyano, m. 146°. <sup>211b</sup>
- 5-phenyl, m. 88°. <sup>149a</sup>
- 5-benzyl, m. 69°. <sup>368</sup>
- 4-Methylamino-5-methyl, m. 58.5–60°; HCl, m. 229°. <sup>144c</sup>
- 4-Diethylamino-5-methyl, m. 76°; HCl, m. 224°. <sup>144c</sup>
- 4-Cyanamino-5-ethoxy, m. 168°. <sup>378a</sup>
- 4-Ureido-5-bromo, m. 167°. <sup>735</sup>
  - 5-ethoxy, m. 167°. <sup>378a</sup>
- 4-(NH:C(OEt)·NH)-5-bromo, m. 110°. <sup>735</sup>
  - 5-ethoxy, m. 77°. <sup>378a</sup>
- 4-Thiocyano-5-methyl, m. 95°. <sup>388</sup>
  - 5-ethyl, m. 47°; b<sub>g</sub> 158–60°. <sup>149b</sup>
  - 5-ethoxy, m. 67°. <sup>378a</sup>
  - 5-bromo, m. 82°. <sup>388</sup>
  - 5-nitro, m. 131°. <sup>688</sup>
  - 5-phenyl, m. 90°; b. 215°. <sup>149a</sup>
- 4-Isothiocyano-5-ethyl, b<sub>g</sub> 146–9°. <sup>149b</sup>
  - 5-bromo, m. 74–80°. <sup>735</sup>
  - 5-phenyl, m. 85°. <sup>149a</sup>
- 4-Thioureido-5-methyl, m. 192°. <sup>738b</sup>
  - 5-ethyl, m. 144°. <sup>149b</sup>
  - 5-bromo, m. 220°. <sup>735</sup>
  - 5-ethoxy, m. 172°. <sup>378a</sup>
- 4-Phenylthioureido-5-ethyl, m. 109°. <sup>149b</sup>
- 4-[ω-Phenylthioureido]-5-bromo, m. 167°. <sup>735</sup>
  - 5-ethoxy, m. 83°. <sup>378a</sup>
- 4-[ω-(3-Nitrophenyl)thioureido]-5-ethoxy, m. 161°. <sup>378a</sup>
- 4-[ω-(4-Methoxyphenyl)thioureido]-5-ethoxy, m. 123°. <sup>378a</sup>
- 4-[ω-(Tolyl)thioureido]-5-ethoxy, *o*-, m. 130°; *p*-, m. 115°. <sup>378a</sup>
- 4-EtO·CS·NH-5-methyl, m. 90°, 88–90°. <sup>379, 738b</sup>
  - 5-ethyl, m. 78°. <sup>149b</sup>
  - 5-bromo, m. 82°. <sup>735</sup>
  - 5-ethoxy, m. 94°. <sup>378a</sup>
- 4-(C<sub>3</sub>H<sub>8</sub>O·CS·NH)-5-ethoxy, m. 57°. <sup>378a</sup>
- 4-EtS·C(OEt):N-5-bromo, m. 43°. <sup>735</sup>
- 4-Acetyldithiourethan-5-ethyl, m. 117°. <sup>149b</sup>
- 4-Anilino-5-ethoxy, m. 60°. <sup>378a</sup>
  - 5-iodo, m. 200° (dec.). <sup>374a, 374b</sup>
- 4-(3-Nitroanilino)-5-ethoxy, m. 125–30°. <sup>378a</sup>
- 4-Toluidino)-5-ethoxy, *o*-, m. 80°; *p*-, m. 106°. <sup>378a</sup>



- 4-(*p*-Anisidino)-5-ethoxy, m. 69°. <sup>378a</sup>
- 4-Methyl-6-ethoxy, b<sub>20</sub> 154°, <sup>354a</sup> b. 287°, b<sub>1</sub> 105–6°; n 22/D 1.5421. <sup>454</sup>
- 6-chloro, b<sub>2</sub> 160°, <sup>142</sup> b<sub>15</sub> 142°. <sup>354a, 377a</sup>
- 6-amino, m. 116°, <sup>354a</sup> 115°; <sup>584</sup> 105°. <sup>142</sup>
- 6-methylamino, m. 87°. <sup>354c</sup>
- 6-ethylamino, m. 70°. <sup>355</sup>
- 6-dimethylcarbamate, b<sub>0.1</sub> 146–80°. <sup>271a</sup>
- 6-thioureido, m. 236°. <sup>469</sup>
- 6-thiocyano, m. 70°; b. 155–8°. <sup>145</sup>
- 6-isothiocyano, b. 146–58° (dec.). <sup>145</sup>
- 6-(EtO)<sub>2</sub>(O)PO, b<sub>0.05</sub> 150–3°. <sup>271b</sup>
- 4-Ethoxy-6-(2-furyl), m. 120°. <sup>28c</sup>
- 4-Formyl-6-chloro, b. 138–9°. <sup>381</sup>
- 4-Chloro-6-(PhN:CH), m. 85°. <sup>381</sup>
- 6-(PhNH·N:CH), m. 147°. <sup>381</sup>
- 4,6-Diamino, m. 146.5°. <sup>574</sup>
- 4-Amino-6-imino, m. 182°. <sup>381</sup>
- 4-Phenyl-6-thiocyano, m. 89°; b<sub>1.5</sub> 204°. <sup>146</sup>
- 6-isothiocyano, b<sub>2</sub> 215–8°. <sup>146</sup>
- 6-thiourea, m. 213°. <sup>146</sup>
- 6-phenylthiourea, m. 216°. <sup>146</sup>
- 6-thionmethylurethan, m. 131°. <sup>146</sup>
- 6-thionethylurethan, m. 116°. <sup>146</sup>
- 6-thionpropylurethan, m. 98°. <sup>146</sup>
- 6-thiobutylurethan, m. 90°. <sup>146</sup>

*Trisubstituted*

- 4,5-Dimethyl-6-chloro, b<sub>2</sub> 129–32°, b<sub>10</sub> 142–4°, <sup>146</sup> b<sub>8</sub> 136–40°; b<sub>18</sub> 162–4°. <sup>147c</sup>
- 6-methoxy, b<sub>5</sub> 138°, b<sub>16</sub> 154°. <sup>147c</sup>
- 6-amino, m. 93°, <sup>167</sup> 90°; <sup>147c</sup> HBr, m. 291° (dec.). <sup>146</sup>
- 6-thiocyano, m. 65.5°; b<sub>1.5</sub> 160°. <sup>146</sup>
- 6-isothiocyano, m. 30°; b<sub>1.5</sub> 150–2°. <sup>146</sup>
- 6-thionmethylurethan, m. 76°. <sup>146</sup>
- 6-thionethylurethan, m. 130°. <sup>146</sup>
- 6-thionpropylurethan, m. 61–3°. <sup>146</sup>
- 6-thiourea, m. 210°. <sup>146</sup>
- 6-phenylthiourea, m. 139–41°. <sup>146</sup>

- 4-Methyl-5-carboxymethyl-6-NH<sub>2</sub>, m. 221°. <sup>372a</sup>  
 -5-ethyl-6-methoxy, b<sub>11</sub> 152-4°, b<sub>22</sub> 162°. <sup>147c</sup>  
 -6-ethoxy, b<sub>6</sub> 139-40°, b<sub>7</sub> 142-5°. <sup>147c</sup>  
 -6-chloro, b<sub>21-3</sub> 177-80°. <sup>302</sup>  
 -6-amino, m. 89-91°. <sup>361</sup>  
 -5-propyl-6-methoxy, b<sub>16</sub> 170-2°. <sup>147a</sup>  
 -6-ethoxy, b<sub>4</sub> 147°. <sup>147a</sup>  
 -6-chloro, b<sub>4</sub> 140-2°, <sup>147a</sup> b. 165-6°. <sup>143</sup>  
 4-Ethoxymethyl-5-ethoxy-6-chloro, b<sub>9-10</sub> 165-6°. <sup>362</sup>  
 4,5,6-Triamino, m. 129°. <sup>574</sup>  
 4-(*p*-Chloroanilino)-4,5-dimethyl, m. 165-6°. <sup>181b, 183</sup>

### 2-R-MERCAPTOPYRIMIDINE AND DERIVATIVES

- 2-Carboxymethyl-4-amino, m. 220°. <sup>322</sup>  
 -4-tetradecylamino, m. 119°. <sup>323a</sup>  
 -4-benzylamino, m. 109-11°. <sup>323a</sup>  
 -4-anilino, m. 197° (dec.); <sup>323a, 622</sup> HCl, m. 250° (dec.). <sup>323a</sup>  
 -4-anisidino, m. 119°. <sup>323a</sup>  
 -4-(1-piperidyl), HCl, m. 199° (dec.). <sup>323a</sup>  
 -4-(4-methylpiperazino), HCl, m. 204° (dec.). <sup>323a</sup>  
 -5-ethoxy, m. 138°. <sup>377a</sup>  
 -4-amino-5-methyl, m. 194°. <sup>322</sup>  
 -6-methyl, m. 256°. <sup>323a</sup>  
 -5-carbethoxy, m. 174-7° (dec.). <sup>360</sup>  
 -4-anilino-5-methyl, HCl salt, m. 210° (dec.). <sup>323a</sup>  
 -6-methyl, m. 189°. <sup>323a</sup>  
 2-Butyl-4-chloro-5-methyl, b<sub>1</sub> 124-6°. <sup>109</sup>  
 -4-amino-5-methyl, m. 86°. <sup>109</sup>  
 2-Octyl-4-chloro-5-methyl, b<sub>2</sub> 144-8°. <sup>109</sup>  
 -4-amino-5-methyl, m. 86°. <sup>109</sup>  
 2-Allyl-4-methyl-6-ethoxy, b<sub>14-18</sub> 168-75°. <sup>370</sup>  
 2-(*p*-Chlorophenyl)-6-Me-4-(2-diethylaminoethylamino), b<sub>0.5</sub> 202-4°; monohydrate, m. 70°. <sup>180</sup>  
 -4-(2-diethylaminopropylamino), b<sub>2</sub> 228-30°. <sup>180</sup>  
 -4-(4-diethylamino-1-methylbutyl, b<sub>0.9</sub> 208-10°. <sup>180</sup>

- 4-(3-dibutylaminopropylamino), m.  
60°;  $b_{0.08}$ ; dipicrate, m. 152°. <sup>180</sup>
- 2-(*p*-Methoxyphenyl)-6-Me-4-(2-diethylaminoethylamino),  $b_1$   
206–8°; monohydrate, m. 83°. <sup>180</sup>
- 4-(2-diethylaminopropylamino),  $b_1$   
228–9°. <sup>180</sup>
- 4-(4-diethylamino-1-methylbutyl),  
 $b_{0.1}$  225.8°. <sup>180</sup>
- 4-(3-dibutylaminopropylamino),  
 $b_{0.09}$  202–4°; dipicrate, m. 154–  
6°. <sup>180</sup>
- 2-Benzyl-4-chloro, m. 49°;  $b_{18}$  210°; HI, m. 136°. <sup>377a</sup>
- 4,6-dimethyl, m. 65–7°. <sup>175, 679</sup>
- 4-amino-6-methyl, m. 113°. <sup>584</sup>
- 6-chloro, m. 104°. <sup>53</sup>
- 6-piperidino, Picrate, m. 195°. <sup>53</sup>
- 5-NO-6-piperidino, m. 153° (dec.). <sup>53</sup>
- 5-formamido-6-piperidino, m. 154°. <sup>53</sup>
- 2-*p*-Chlorobenzyl-4,6-dimethyl, m. 56.5°. <sup>175, 679</sup>
- 2-*p*-Nitrobenzyl-4,6-dimethyl, m. 113.5°. <sup>175</sup>
- 4-methyl-6-ethoxy, m. 104°. <sup>330</sup>
- 6-allyloxy, m. 78°. <sup>330</sup>
- 2-Phenacyl-4-methyl-6-methoxy, m. 144°. <sup>382b</sup>
- 6-ethoxy, m. 86–8°. <sup>382b</sup>
- 6-phenacyloxy, m. 119°. <sup>382a</sup>

## 2-METHYLTHIO-4-PYRIMIDONE AND DERIVATIVES

Unsubstituted, m. 199°; <sup>494a, 377c, 742</sup> HCl, m. 189°. <sup>735</sup>

### *Monosubstituted*

- 5-Methyl, darkens 225° m. 233°. <sup>742</sup>
- 5-Carboxy, m. 235°. <sup>739</sup>
- 5-Ethoxy, m. 190°. <sup>378b</sup>
- 5-Bromo, m. 239° (dec.). <sup>377a</sup>
- 5-Fluoro, sublimes 140–50° m. 241–3°. <sup>222, 313b, 327</sup>
- 5-Benzyl, m. 178°. <sup>282</sup>
- 6-Methyl, m. 219°; <sup>584, 585c</sup> 220°, <sup>116</sup> 224–6°. <sup>659, 742</sup>
- 6-Furylmethyl, m. 160°. <sup>28b</sup>
- 6-Ethyl, m. 152°, 153°. <sup>659</sup>
- 6-Propyl, m. 154°; <sup>668a</sup> 155°. <sup>659</sup>

- 6-Butyl, m. 127°. <sup>659</sup>  
 6-Hydroxy, m. 300°. <sup>736</sup>  
 6-Amino, m. 262° (dec.), <sup>52</sup> 267° (dec.). <sup>356b, 374a, 374b</sup>  
 6-Phenyl, m. 240°. <sup>659</sup>  
 6-Benzyl, m. 180°. <sup>659</sup>  
 6-(2-Furyl), m. 265°, 267°. <sup>28c</sup>

### Disubstituted

- 3-Methyl-5-COOMe, m. 153°. <sup>745a</sup>  
 3-Methoxyethyl-5-acetyl, m. 94°. <sup>745a</sup>  
 3-Phenyl-5-carbethoxy, m. 128°. <sup>745a</sup>  
 3,6-Dimethyl, <sup>299</sup> m. 94°. <sup>427c, 681, 741a</sup>  
 3-Methyl-6-amino, m. 257°; Ac, m. 251°. <sup>576</sup>  
 5,6-Dimethyl, m. 225-7°. <sup>146</sup>  
 5-Methyl-6-carboxy, m. 244°; Et ester, m. 202°. <sup>358b</sup>  
     -6-hydroxy, m. 303° (dec.). <sup>736</sup>  
 5-Carboxymethyl-6-methyl, sinters 260° m. 270° (dec.). <sup>372a</sup>  
 5-Ethyl-6-methyl, chars 201-2°, m. 203°. <sup>742</sup>  
     -6-hydroxy, m. 257°. <sup>736</sup>  
 5-Propyl-6-methyl, m. 181°. <sup>143</sup>  
 5-Butyl-6-methyl, m. 129°. <sup>142</sup>  
 5-Allyl-6-methyl, m. 189-91°. <sup>373</sup>  
 5-Bromo-6-methyl, m. 249° (dec.). <sup>494b</sup>  
     -6-amino, sinters 200°, not melted at 300°. <sup>374b</sup>  
 5-Fluoro-6-fluoromethyl, m. 222° (dec.). <sup>222</sup>  
     -6-COOH, m. 199-201° (PhMe). <sup>327</sup>  
 5,6-Diamino, m. 211° (dec.), <sup>355</sup> 216°. <sup>375</sup>  
 5-Nitroso-6-amino, m. 255° (dec.). <sup>355</sup>  
 5-Nitro-6-amino, m. 299°; Na salt m. 333°. <sup>27</sup>  
 5-(3-Methyl-2-thioureido)-6-NH<sub>2</sub>, (0.5 mol H<sub>2</sub>O) m. 225-8°. <sup>169</sup>  
 5-Phenylazo-6-amino, m. 290° (dec.). <sup>583</sup>  
 5,6-*c*-Penteno, m. 270-2°. <sup>184</sup>  
 5,6-*c*-Hexeno, m. 220-2°. <sup>184</sup>

### Trisubstituted

- 3,5-Dimethyl-6-amino, m. 173°; Ac, m. 147°. <sup>576</sup>  
 3,6-Dimethyl-5-iodo, m. 219°. <sup>29a</sup>  
 3-Methyl-5,6-diamino, m. 212°. <sup>356b</sup>  
     -5-phenylazo-6-amino, m. 250°. <sup>583</sup>

## 2-ETHYLTHIO-4-PYRIMIDONE AND DERIVATIVES

Unsubstituted,<sup>738a</sup> m. 149°;<sup>740c</sup> 152°.<sup>372, 742</sup>

*Monosubstituted*

1-Carboxymethyl, m. 209°; Et ester, m. 129°.<sup>740b</sup>

1-Benzyl, m. 139°.<sup>367</sup>

3-Methyl, m. 80°.<sup>372a</sup>

3-Benzyl, m. 77°.<sup>367</sup>

5-Methyl, m. 159°.<sup>377c, 738b</sup>

5-Carboxymethyl, m. 184° (dec.);<sup>358b, 387, 740a</sup> Et ester, m. 147°.<sup>387, 740a</sup>

5-Ethyl, m. 120°.<sup>149b</sup>

5-Ethoxy,<sup>377c</sup> m. 169°.<sup>378b</sup>

5-Carboxy, m. 167° (cir); Et ester, m. 131°.<sup>739</sup>

5-Bromo, m. 189°.<sup>738b</sup>

5-Iodo, m. 196°.<sup>374a, 374b</sup>

5-Fluoro, m. 190° (EtOAc-10°),<sup>327</sup> 193° (dec.).<sup>222</sup>

5-Amino, m. 160°.<sup>358b</sup>

5-Methylamino, m. 222°.<sup>445</sup>

5-Cabethoxyamino, m. 190°.<sup>358b</sup>

5-Carbethoxyaminomethyl, m. 149.5°.<sup>445</sup>

5-Carbamino, m. 214° (dec.).<sup>740a</sup>

5-Cyano, m. 222°,<sup>211b, 358a</sup>

5-PhCO·NH, m. 239°.<sup>365b</sup>

5-Ph·CH<sub>2</sub>O·CO·NH, m. 160°.<sup>445</sup>

5-PhCH:N, m. 185°.<sup>358b</sup>

5-Phthalimido, m. 231°.<sup>365b</sup>

5-Phenyl, m. 158°.<sup>735</sup>

5-Phenoxy, m. 159°.<sup>375</sup>

5-Benzyl, m. 139°.<sup>367</sup>

6-Methyl, m. 145°,<sup>444</sup> 145-7°.<sup>354a</sup>

6-Carboxymethyl, m. 155°; Et ester, m. 131°.<sup>740a, 740b</sup>

6-Furylmethyl, m. 137°.<sup>28b</sup>

6-Ethyl, m. 89°.<sup>735</sup>

6-Amino, m. 219°,<sup>586</sup> 217°.<sup>374a, 374b</sup>

6-(2-Furyl), m. 229°.<sup>28c</sup>

*Disubstituted*

1,5-Dimethyl, m. 156°.<sup>365a</sup>

- 1-Methyl-5-ethoxy, m. 149–51°. <sup>376b</sup>  
 1-Benzyl-5-methyl, m. 122°. <sup>367</sup>  
     -5-bromo, m. 129°. <sup>367</sup>  
     -5-ethoxy, m. 86°. <sup>376a</sup>  
 3,5-Dimethyl, m. 65°. <sup>365a</sup>  
 3-Methyl-5-ethoxy, m. 50°. <sup>376b</sup>  
 3-Benzyl-5-methyl, m. 70°. <sup>367</sup>  
     -5-ethoxy, m. 141°. <sup>376a</sup>  
 3,6-Dimethyl, m. 64°. <sup>377c</sup>  
 3-Methyl-6-amino, m. 204°. <sup>574</sup>  
 3-Ethyl-6-methyl, b. 288° (partial dec.), b<sub>1</sub> 106°; n<sub>D</sub> 22/D 1.5523. <sup>454</sup>  
 3-Benzyl-6-methyl, m. 228°. <sup>741a</sup>  
 5,6-Dimethyl, m. 156°. <sup>820, 147c</sup>  
 5-Methyl-6-diethoxymethyl, m. 100°. <sup>366a</sup>  
     -6-[(CH<sub>3</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>]<sub>2</sub>CH, m. 219°. <sup>358c</sup>  
     -6-carboxy, m. 220°; Et ester, m. 173°. <sup>379</sup>  
     -6-formyl, m. 186°. <sup>366a</sup>  
     -6-PhNH·N:CH, softens 201° (dec.) 238°. <sup>366a</sup>  
     -6-[NOH:CH], m. 235°. <sup>366a</sup>  
 5-Carboxymethyl-6-methyl, m. 255°; Et ester, m. 163–5°. <sup>372a</sup>  
 5-Ethyl-6-methyl, m. 141°, <sup>147c</sup> 138°. <sup>361</sup>  
 5-Propyl-6-methyl, m. 93°. <sup>143, 147a</sup>  
 5-Butyl-6-methyl, m. 93°. <sup>142</sup>  
 5-Bromo-6-ethyl, m. 173°. <sup>735</sup>  
 5-Fluoro-6-carbethoxy, m. 169°. <sup>222, 327</sup>  
 5,6-Diamino, m. 195°. <sup>586</sup>  
 5-Benzyl-6-methyl, m. 166°. <sup>741a</sup>  
 5-Phenoxy-6-phenoxyethyl, m. 170°. <sup>373</sup>  
 5,6-Di-(β-naphthoxy), m. 198°. <sup>373</sup>  
 5-Phenylazo-6-amino, m. 285°. <sup>583</sup>

### Trisubstituted

- 3-Methyl-5,6-diamino, Hemihydrate, m. 98°. <sup>574</sup>  
 3-Benzyl-5-methyl-6-carbethoxy, m. 69–71°. <sup>389</sup>

### 2-R-THIO-4-PYRIMIDONE AND DERIVATIVES

- 2-Carboxymethyl, m. 178°, <sup>740c</sup> Et ester,  $\frac{1}{2}$ H<sub>2</sub>O, m. 155°. <sup>386a, 740c</sup>  
     -6-methyl, m. 192–7°, <sup>386a</sup> 204°; <sup>444</sup> Et ester, m. 146°, <sup>386a, 386b</sup>  
     143°. <sup>444</sup>  
     -6-ethyl, m. 170°. <sup>158b, 212</sup>

- 6-propyl, m. 152°; 158a, 158b, 212 Aminothiazole salt, m. 123°.<sup>212</sup>  
 Et ester, m. 119°.<sup>158b, 212</sup>
- 6-benzyl, m. 154°.<sup>158b, 212</sup>
- 3-Me-5-OH, m. 217° (dec.).<sup>376b</sup>
- 5,6-dimethyl, m. 129°; Et ester, m. 133°.<sup>146</sup>
- 2-Carbethoxymethyl-6-amino, m. 180° (dec.).<sup>27</sup>  
 -5-Bu-6-Me, m. 111°.<sup>142</sup>
- 2-Dicarbethoxymethyl-6-amino, m. 173° (dec.).<sup>27</sup>
- 2-Propyl, m. 170°.<sup>735</sup>
- 6-furylmethyl, m. 100°.<sup>28b</sup>
- 6-(2-furyl), m. 225°.<sup>28c</sup>
- 5-Pr-6-Me, m. 90°.<sup>143</sup>
- 2-*i*-Propyl-6-propyloxy, m. 100°.<sup>28c</sup>  
 -6-(2-furyl), m. 245°.<sup>28c</sup>
- 2,5-*c*-Propyl-6-methyl, m. 225-7°.<sup>373</sup>
- 2-(β,γ-Dibromopropyl-5-Br-6-Me, m. 160-5° (dec.).<sup>370</sup>
- 2-Butyl-5-methyl, m. 106°.<sup>109</sup>
- 2-*i*-Butyl, m. 107°.<sup>735</sup>
- 2-*i*-Amyl, m. 115°.<sup>735</sup>
- 2-Octyl-5-methyl, m. 89°.<sup>109</sup>
- 2-Allyl-6-methyl, m. 131°,<sup>370</sup> 133°.<sup>299</sup>  
 -3,6-dimethyl, m. 43°.<sup>370</sup>  
 -3-PhCH<sub>2</sub>-6-Me, b<sub>14-15</sub> 225-35°.<sup>370</sup>  
 -5-I-6-Me, m. 159°.<sup>299</sup>
- 2-HOOC·ME·CH-6-Pr, m. 148°; Et ester, m. 102°.<sup>158b, 212</sup>
- 2-HOOC·CH<sub>2</sub>CH<sub>2</sub>-6-Pr, m. 152-4°.<sup>158b, 212</sup>
- 2-HOOC·C·(Me)<sub>2</sub>-6-Pr, m. 146°; Et ester, m. 90°.<sup>158b, 212</sup>
- 2-HOOC·CH·(CHMe<sub>2</sub>)-6-Pr, m. 154°.<sup>158b, 212</sup>
- 2-CH<sub>3</sub>·CO·CH<sub>2</sub>-6-methyl, m. 152°.<sup>382a</sup>
- 2-CH<sub>3</sub>·C(:NOH)·CH<sub>2</sub>-6-methyl, m. 162° (dec.).<sup>382a</sup>
- 2-HOOC·CO·CHCH<sub>2</sub>, m. 201° (dec.).<sup>386a</sup>  
 -6-methyl, m. 210-2°.<sup>386b</sup>
- 2-HOOC·C(:NOH)·CH<sub>2</sub>-6-methyl, m. 161°.<sup>386b</sup>
- 2-Ph·CO·CH<sub>2</sub>-6-methyl, m. 175°; Na salt, m. 206° (dec.).<sup>382a</sup>  
 -3,6-dimethyl, m. 155°.<sup>382a</sup>
- 2-Ph·C(:NOH)·CH<sub>2</sub>-6-methyl, m. 183°.<sup>382a</sup>
- 2-Ph·NH·N:C<sub>6</sub>H<sub>5</sub>·C·CH<sub>2</sub>-6-methyl, m. 295°.<sup>382a</sup>
- 2-(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>·COCH<sub>2</sub>)-6-methyl, m. 195°.<sup>383</sup>
- 2-EtOOC·(HOHC:)C, m. 138-40°.<sup>386a</sup>  
 -6-methyl, m. 106°.<sup>386a</sup>
- 2-EtOOC·CO·(COOEt)CH, m. 171°.<sup>386a</sup>

- 2-HOOC·CO(COOH)·CH-6-methyl, m. 159–61°; <sup>386b</sup> diEt ester, m. 140°.<sup>386a, 386b</sup>  
 2-HOOC·C(:NOH)·(COOH)CH-6-methyl, Na salt, m. 200°.<sup>386b</sup>  
 2-Ph<sub>2</sub>CH-6-methyl, m. 214°.<sup>361</sup>  
 2-(4-Ethoxyphenyl)-5,6-dimethyl, m. 216°.<sup>577</sup>  
 2-Benzyl, m. 193°.<sup>377a, 740c</sup>  
   -1-benzyl, m. 145°.<sup>377a</sup>  
   -5-methyl, m. 205°.<sup>741b</sup>  
   -5-fluoro, m. 216–8° (EtOH).<sup>327</sup>  
   -6-methyl, m. 176–8°.<sup>208</sup>  
   -6-furylmethyl, m. 150°.<sup>28b</sup>  
   -6-amino, m. 243.5°.<sup>53</sup>  
   -6-(2-furyl), m. 210°.<sup>28c</sup>  
   -5-Et-6-Me, m. 160°.<sup>361</sup>  
   -5-PhCH<sub>2</sub>-6-Me, m. 194°.<sup>741a</sup>  
 2-(4-Nitrobenzyl)-6-methyl, m. 220°.<sup>330</sup>  
   -3,6-dimethyl, m. 136°.<sup>330</sup>  
 2-(4-Cyanobenzyl)-6-methyl, m. 240°.<sup>60</sup>  
 2-(2-Thienyl)-6-methyl, m. 161°.<sup>408</sup>

### *Dihydrothiopyrimidines*

- 2-Thio-1-benzyl-4-phenyl, m. 161°.<sup>132</sup>  
 2-Thio-3,4,6-trimethyl, m. 156.5°.<sup>302</sup>  
 2-Mercapto-1-phenyl, m. 151°.<sup>761</sup>  
 2-Mercapto-1-phenyl-4-Me-4,6-diethyl, m. 182°.<sup>23</sup>  
 2-Methylmercapto-4,5-dibromo, m. 65–75°.<sup>377b</sup>  
 2-Ethylmercapto-4,5-dibromo, HBr, m. 180° (dec.).<sup>377b</sup>  
   -4-imino-5-carbethoxy, m. 102°.<sup>737a</sup>  
   -5-[H<sub>2</sub>N·CO], m. 219°.<sup>737a</sup>  
   -4-chloro-5-[Cl<sub>2</sub>OP·N:], m. 247–50°.<sup>358b</sup>  
   -5-[(H<sub>2</sub>N)<sub>2</sub>P·N:], m. 290–300°.<sup>358b</sup>

### 2-MERCAPTO-4,4,6-TRIMETHYL-1,4-DIHYDROPYRIMIDINES

- Unsubstituted, m. 249°, <sup>703</sup> 253°, <sup>225</sup> 267°, <sup>23</sup> 255°.<sup>493</sup>  
 1-Carboxymethyl, m. 176°.<sup>492a</sup>  
 1-(2-Hydroxyethyl), m. 186°; <sup>686</sup> 180°.<sup>493</sup>  
 1-HOOC·CH<sub>2</sub>·CH<sub>2</sub>, m. 143°.<sup>492a</sup>  
 1-HOOC·CH·CH<sub>3</sub>, m. 192°.<sup>492a</sup>  
 1-*i*-Propyl, m. 267°.<sup>493, 686</sup>  
 1-*c*-Hexyl, <sup>686</sup> m. 282°.<sup>493</sup>



- 1-Allyl, m. 130°. <sup>704</sup>  
 1-Amino, m. 210°. <sup>492b</sup>  
 1-Phenyl, m. 192°, <sup>23, 703</sup> 193°, <sup>493</sup> 187°. <sup>686</sup>  
 1-(Tolyl), *o*-, m. 201–3°, <sup>686</sup> 202°; *p*-, m. 191°. <sup>493</sup>  
 1-(*p*-HOC<sub>6</sub>H<sub>4</sub>), m. 212°. <sup>23</sup>  
 1-(HOOC·C<sub>6</sub>H<sub>4</sub>), *o*-, m. 210°; <sup>23, 492a</sup> Me ester, m. 186°; <sup>492a</sup> *p*-, m. 209°. <sup>23, 492a</sup>  
 1-(ClC<sub>6</sub>H<sub>4</sub>), *o*-, m. 212°; *p*-, m. 200°. <sup>23</sup>  
 1-(2,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), m. 206°. <sup>23</sup>  
 1-(*p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>), m. 192°. <sup>23</sup>  
 1-PhNH, m. 192°, <sup>23</sup> 171°. <sup>492b</sup>  
 1-(*p*-NH<sub>2</sub>·SO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>), m. 210°. <sup>23</sup>  
 1-[*p*-(6-Me-2-benzothiazolyl) phenyl], m. 215°. <sup>23</sup>  
 1-(Naphthyl),  $\alpha$ -, <sup>612</sup> m. 216°; <sup>493</sup>  $\beta$ -, m. 204°. <sup>23</sup>

## BIS (2-MERCAPTO-4,4,6-TRIMETHYL-1,3-DIHYDROPYRIMIDINES

- 1,1'-Ethylene, m. 200°. <sup>686</sup>  
 1,1'-(Phenylene), *m*-, m. 171–4°; <sup>686</sup> 202°; <sup>493</sup> *p*-, m. 225°. <sup>23</sup>  
 1,1'-(*p*-Anilino), m. 245°. <sup>23</sup>

## TETRAHYDROPYRIMIDINES

- 2-Thio-4-Me-4,6-diphenyl, m. 172–4°. <sup>224</sup>  
     -5-thioureido-6-Me, m. 175°. <sup>561</sup>  
 2-Mercapto, m. 198°, <sup>436</sup> 207°. <sup>637, 678</sup>  
     -1-phenyl, m. 215°. <sup>285</sup>  
     -1-*p*-tolyl, m. 188°. <sup>256</sup>  
 2-Methylmercapto-4-imino-6-methoxy, m. 255°. <sup>356b</sup>  
     -4,5-dioxy-5-amino, m. 301°. <sup>736</sup>

## HEXAHYDROPYRIMIDINES

- 4,6-Diimino-5-ethyl, m. 292°. <sup>240c</sup>  
     -5,5-diethyl, m. 230° (dec.). <sup>240b, 240c</sup>  
     -5,5-dipropyl, m. 227°. <sup>225</sup>

## 2-THIOHYDROURACILS

- 6-Carboxy, m. 243° (dec.). <sup>561</sup>  
 6-Phenyl, m. 240–2°. <sup>580a</sup>  
 6-(2-Naphthyl), m. 262.5°. <sup>616</sup>  
 6-Benzylidene, m. 217°. <sup>439c</sup>  
 3-Methyl-6-benzylidene, m. 176°. <sup>439c</sup>

- 3-Ethyl-6-benzylidene, m. 237–40°. <sup>439c</sup>  
 5-Methyl-6-phenyl, m. 186°. <sup>580b</sup>  
 5-Oximino-6-imino. <sup>240b</sup>  
 5,5-Dimethyl-6-imino, m. 215°. <sup>240a</sup>  
 5-Methyl, 5-Phenyl-6-keto, m. 210°. <sup>100</sup>  
 5-*i*-Propyl, 5-Phenyl-6-keto, m. 187°. <sup>100</sup>  
 5-*c*-Hexyl, 5-Ethyl-6-keto, m. 189°. <sup>100</sup>  
 5-*c*-Hexyl, 5-Propyl-6-keto, m. 142–4°. <sup>100</sup>

#### 4-MERCAPTOPYRIMIDINE AND DERIVATIVES

- Unsubstituted, m. 230°; <sup>585a</sup> HCl, m. 220° (dec.). <sup>94a, 468</sup>  
 2-Methylamino, m. 80°; 1-Methiodide, m. 174–6°. <sup>6, 7</sup>  
 5-Amino, m. 207° (dec.). <sup>345</sup>  
 6-Methyl, sinters from 180° m. 255° (dec.). <sup>267</sup>  
 2-Ethoxy-5-nitro, m. 133°. <sup>688</sup>  
     -5-amino, m. 127°. <sup>688</sup>  
 2-Chloro-5-amino, m. 300°. <sup>345</sup>  
 2,5-Diamino, m. 235°. <sup>688</sup>  
 2-Amino-5(*p*-Chlorophenoxy), m. 250°. <sup>239a</sup>  
 2-Anilino-5-amino, m. 218° (dec.). <sup>688</sup>  
 2,6-Dimethyl, m. 200° (dec.), <sup>585b</sup> 230°. <sup>640</sup>  
 2,6-Diamino, m. 309–11°. <sup>229</sup>  
 2-Amino-6-methyl, sublimes. <sup>267</sup>  
 2-Benzamino-6-methyl, m. 198°. <sup>267</sup>  
 2-(*p*-Tolyl)-6-methyl, m. 114°. <sup>388</sup>  
 5,6-Dimethyl, sinters from 200°, m. 265°. <sup>639</sup>  
 5-Amino-6-chloro, m. 190–200° (dec.). <sup>478</sup>  
 5-Formamido-6-amino, m. 255°. <sup>229</sup>  
 2,5-Diamino-6-methyl, m. 310° (dec.). <sup>619b</sup>  
 2,6-Diamino-5-formamido, m. 275° (dec.). <sup>229</sup>  
 2-Amino-5,6-dimethyl, m. 270°. <sup>639</sup>  
     -5-ethyl-6-methyl, m. 230–45°. <sup>119</sup>  
     -5-*p*-chlorophenyl-6-ethyl, m. 231°. <sup>324</sup>

#### 4-METHYLMERCAPTOPYRIMIDINE AND DERIVATIVES

- 2-Chloro, *b*<sub>15</sub> 126°. <sup>6, 7</sup>  
 2-Chloro-6-methyl, *b*<sub>70</sub> 166–8°. <sup>6, 7</sup>  
 2-Amino-6-methyl, m. 154.5°; <sup>46a</sup> 3 methiodide, m. 262° (dec.);  
     1-Methiodide, m. 225–7° (dec.). <sup>9</sup>  
 2-Ethylamino-6-methyl, m. 62°; 1-methiodide, m. 226°. <sup>6, 7</sup>  
 2-Sulfanilamido-6-Me, m. 198.5°. <sup>46a</sup>

- 2-(*p*-Nitrophenylsulfonamido)-6-Me, m. 217–22°. <sup>46a</sup>  
 2-[3-(*p*-chlorophenyl)guanidino]-6-Me, m. 147–9°. <sup>186</sup>  
 5-Amino-6-chloro, m. 94–6°. <sup>478</sup>  
 2-Chloro-5-amino-6-methyl, m. 110°. <sup>610b</sup>  
     -5-nitro-6-methyl, m. 69°. <sup>619b</sup>  
 2-Amino-5-*p*-chlorophenyl-6-ethyl, m. 196°. <sup>324</sup>

## 4-R-MERCAPTOPYRIMIDINE AND DERIVATIVES

- 4-Ethyl-2-Amino, m. 157°, 2-sulfanilamido, m. 264°; Ac, m. 269°. <sup>102</sup>  
     -2,5-diamino, m. 87°. <sup>688</sup>  
     -2-chloro-5-amino, m. 194°. <sup>345</sup>  
     -2-[2-Et<sub>2</sub>N·CH<sub>2</sub>CH<sub>2</sub>·NH<sub>2</sub>]-6-Me, m. 240°; Picrate, m. 158°. <sup>296</sup>  
 4-CH<sub>3</sub>·C(OH)-2,5-diamino-6-methyl, m. 230°. <sup>619b</sup>  
 4-Phenyl-6-Me-2-amino, m. 190.5°. <sup>46b</sup>  
     -2-(*p*-O<sub>2</sub>N·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·NH), m. 223–7°. <sup>46b</sup>  
     -2-(*p*-H<sub>2</sub>N·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·NH), m. 151.5°, 139–41°, m. again at 189–90°; Ac, m. 221.5°. <sup>46b</sup>  
 4-(*p*-Chlorophenyl)-6-Me-2-[2-(Et)<sub>2</sub>N·C<sub>2</sub>H<sub>4</sub>], m. 85°; b<sub>0.1</sub> 201–12°. <sup>180</sup>  
     -2-[3-Et<sub>2</sub>N·C<sub>3</sub>H<sub>6</sub>·NH], b<sub>0.7</sub> 228–30°. <sup>180</sup>  
     -2-[4-Et<sub>2</sub>N-1-(CH<sub>3</sub>)C<sub>4</sub>H<sub>8</sub>·NH], b<sub>3</sub> 224–6°. <sup>180</sup>  
 4-(*p*-Methoxyphenyl)-6-Me-2-[2-Et<sub>2</sub>N·C<sub>2</sub>H<sub>4</sub>·NH], m. 69°; b<sub>0.8</sub> 212–4°. <sup>180</sup>  
     -2-[3-Et<sub>2</sub>N·C<sub>3</sub>H<sub>6</sub>·NH], b<sub>2</sub> 228–30°. <sup>180</sup>  
     -2-[4-Et<sub>2</sub>N-(CH<sub>3</sub>)·C<sub>4</sub>H<sub>8</sub>·NH], b<sub>1.5</sub> 210–12°. <sup>180</sup>  
 4-Benzyl purine monohydrate, m. 189° (dec.). <sup>229</sup>  
 4-Benzyl-6-methyl, m. 60°; 1-methiodide, m. 154°. <sup>6, 7</sup>  
     -2,6-dihydroxy, m. 184°. <sup>208</sup>  
     -5,6-diamino (monohydrate), m. 104–6°; 5-formamido, m. 203°. <sup>229</sup>  
     -2,5-diamino-6-methyl, m. 160°. <sup>619b</sup>  
     -2-amino-5-nitro-6-methyl, m. 155°. <sup>619b</sup>  
 4-Benzoyl-2-amino-6-methyl, m. 130–3°. <sup>267</sup>

## 4-R-THIO-2-PYRIMIDONES AND DERIVATIVES

- 4-Methyl, m. 205°. <sup>738c</sup>  
 4-Methyl-1-methyl, m. 124°. <sup>738c</sup>  
     -3-benzyl, m. 146–8°. <sup>738c</sup>  
     -5-methyl, m. 205–11°. <sup>741b</sup>

- 6-hydroxy, m. 222°. <sup>208</sup>
- 1,5-dimethyl, m. 83°. <sup>741b</sup>
- 1,6-dimethyl, m. 171°. <sup>741a</sup>
- 5-amino-6-hydroxy, m. 253° (dec.); 5-ureido, m. 350° (dec.). <sup>246</sup>
- 4-(2-Nitrobenzyl)-6-methyl, m. 208°. <sup>741a</sup>
- 4-(2,4-Dinitrophenyl)-6-methyl, m. 175°. <sup>741a</sup>

## 2-R-4-R'-DIMERCAPTOPYRIMIDINES AND DERIVATIVES

R	R'
2-H	-4-Et, b <sub>6</sub> 135-7°; n 24/D 1.5974. <sup>146</sup> -5-methyl, b <sub>11</sub> 158-60°; n 23/D 1.5900. <sup>146</sup> -5- <i>p</i> -chlorophenyl, m. 317°. <sup>324</sup>
2-Me	-4-H-5-ethoxy, m. 190°. <sup>368</sup> -6-methyl, m. 214°. <sup>585a, 585b, 741a</sup> -4-Me-6-hydroxy, m. 150.5°. <sup>208</sup> -5-NH <sub>2</sub> -6-Me, m. 75°. <sup>619b</sup>
2-Et	-4-H, m. 149°. <sup>740c</sup> -5-methyl, m. 180°, 181°. <sup>388, 741b</sup> -5-ethoxy, m. 145°. <sup>378a</sup> -5-bromo, m. 198°. <sup>735</sup> -5-phenyl, m. 171-6°. <sup>149a</sup> -6-methyl, m. 205°. <sup>585b</sup> -6-phenyl, m. 207°. <sup>146</sup> -5,6-dimethyl, m. 188°. <sup>146</sup> -4-Et-5-NH <sub>2</sub> -6-Me. <sup>619b</sup>
2-HOOC·CH <sub>2</sub>	-4-HOOC·CH <sub>2</sub> , m. 200° (dec.). <sup>740c</sup>
2-PhCH <sub>2</sub>	-4-PhCH <sub>2</sub> -6-hydroxy, m. 147°. <sup>208</sup>

## 4-R-6-R'-DIMERCAPTOPYRIMIDINES AND DERIVATIVES

R	R'
4-H	-6-H-2-amino, m. 260°, <sup>585b</sup> 250°. <sup>585a</sup> -5-amino, m. 330°. <sup>189</sup>
4-Et	-6-Et-2-amino, m. 53°; 2-sulfanilamido, m. 162°; Ac, 192°. <sup>102</sup>
4-H	-6-PhCH <sub>2</sub> -5-amino, m. 183°. <sup>345</sup>

## 5-R-MERCAPTOPYRIMIDINES AND DERIVATIVES

- 5-(*p*-Nitrophenyl-NH)-4-OH-6-Me, m. 234°. <sup>335</sup>
- 4,6-dimethyl, m. 196°. <sup>335</sup>

5-Benzyl-2,4-dihydroxy, m.  $290^{\circ}$ .<sup>368</sup>  
 -2-OH-4-NH<sub>2</sub>, m.  $240-1^{\circ}$ .<sup>368</sup>

## 2-R-5-R'-DIMERCAPTOPYRIMIDINES AND DERIVATIVES

R	R'
2-H	-5-Benzyl-4-OH, m. $196^{\circ}$ . <sup>368</sup>
2-Ethyl	-5-benzyl-4-Cl, m. $48^{\circ}$ . <sup>368</sup>
	-4-OH, m. $156^{\circ}$ . <sup>368</sup>
	-4-NH <sub>2</sub> , m. $69^{\circ}$ . <sup>368</sup>

## 2-THIOURACIL AND DERIVATIVES

Unsubstituted,<sup>377c, 735</sup> m.  $280^{\circ}$  (dec.);<sup>10</sup>  $304^{\circ}$  (dec.);<sup>654</sup>  $340^{\circ}$ .<sup>29a, 386a, 740c</sup>

*Monosubstituted*

1-Methyl, m.  $228^{\circ}$ .<sup>654</sup>  
 1-c-Hexyl, m.  $296-8^{\circ}$ .<sup>689</sup>  
 1-Phenyl, m.  $236^{\circ}$ .<sup>654</sup>  
 3-*i*-Butyl, m.  $189^{\circ}$ .<sup>745a</sup>  
 3-Amyl, m.  $196^{\circ}$ .<sup>745a</sup>  
 3-*i*-Amyl, m.  $184^{\circ}$ .<sup>745a</sup>  
 3-Benzyl, m.  $231^{\circ}$ .<sup>377a</sup>  
 5-Ethyl, m.  $190-2^{\circ}$ .<sup>299</sup>  
 5-*n*-Propyl, m.  $161-3^{\circ}$ .<sup>299</sup>  
 5-*i*-Propyl, m.  $242-4^{\circ}$ .<sup>299</sup>  
 5-*n*-Butyl, m.  $151.5^{\circ}$ ,  $153.5^{\circ}$ .<sup>299</sup>  
 5-Chloro, m.  $262-6^{\circ}$  (dec.).<sup>430a</sup>  
 5-Iodo, m.  $228-38^{\circ}$  (dec.);<sup>430b</sup>  $219-21^{\circ}$  (dec.);<sup>430a</sup> mono sodium salt, monohydrate, m.  $235^{\circ}$  (dec.).<sup>430b</sup>  
 5-Fluoro, m.  $227-9^{\circ}$  (dec.);<sup>222</sup>  $226^{\circ}$ .<sup>313a, 327</sup>  
 5-Benzamino, m.  $300-10^{\circ}$  (dec.).<sup>358b</sup>  
 5-Cyano, m.  $285^{\circ}$  (dec.).<sup>43, 299</sup>  
 5-Acetylhydrazide, m.  $208^{\circ}$ .<sup>445</sup>  
 5-Me isocyanate, m.  $189-91^{\circ}$  (dec.).<sup>445</sup>  
 5-Methylurea, m.  $190-2^{\circ}$ .<sup>445</sup>  
 5-Methylphenylurea, m.  $224^{\circ}$ .<sup>445</sup>  
 5-[*p*-Chlorophenyl], m.  $335-7^{\circ}$  (dec.).<sup>623</sup>  
 5-[3,4-Dichlorophenyl], m.  $305-9^{\circ}$  (dec.),  $308-11^{\circ}$  (dec.).<sup>623</sup>  
 5-Benzyl, m.  $208^{\circ}$ .<sup>282</sup>  $290^{\circ}$ .<sup>368</sup>  
 5-Phenoxy, m.  $254^{\circ}$ .<sup>368</sup>

- 5-(Chlorophenoxy), *o*-, m. 268–70°; *p*-, m. 268°. <sup>239b</sup>  
 5-(*p*-Bromophenoxy), m. 285°. <sup>239b</sup>  
 5-(*p*-Iodophenoxy), m. 275°. <sup>239b</sup>  
 5-(2,4-Dichlorophenoxy), m. 267°. <sup>239b</sup>  
 5-(2,4-Dibromophenoxy), m. 271°. <sup>239b</sup>  
 5-(2,4,5-Trichlorophenoxy), m. 310°. <sup>239b</sup>  
 5-(3,4-Methylchlorophenoxy), m. 250–2°. <sup>239b</sup>  
 5-(*m*-Methylphenoxy), m. 253°. <sup>239b</sup>  
 5-(3,4-Dimethylphenoxy), m. 250–5°. <sup>239b</sup>  
 5-[*p*-(Me<sub>3</sub>C)-phenoxy], m. 267°. <sup>239b</sup>  
 5-(*p*-Methoxyphenoxy), m. 174–8°. <sup>239b</sup>  
 5-[(*p*-EtOOC)phenoxy], m. 242–6°. <sup>239b</sup>  
 5-[2,4-Cl(Me<sub>3</sub>C)phenoxy], m. 206–8°. <sup>239b</sup>  
 5-[4,5,2-ClMe(Me<sub>2</sub>CH)phenoxy], m. 244–51°. <sup>239b</sup>  
 5-[(3,4-CH:CH:CH:CH)phenoxy], m. 250–70°. <sup>239b</sup>  
 5-(*p*-Phenylphenoxy), m. 298–301°. <sup>239b</sup>  
 5-[(*p*-PhCH<sub>2</sub>O)phenoxy], m. 245–55°. <sup>239b</sup>  
 5-(*p*-Chlorobenzyl), m. 267°. <sup>239b</sup>  
 5-[(*p*-Me<sub>2</sub>N)benzyl], m. 210°. <sup>239b</sup>  
 5-(*p*-Methoxybenzyl), m. 223°. <sup>239b</sup>  
 5-(*p*-Methylbenzyl), m. 240–3°. <sup>239b</sup>  
 5-[3,4-MeO(PhCH<sub>2</sub>O)benzyl], m. 210–11°. <sup>239b</sup>  
 6-methyl, m. 320°, <sup>29a, 299</sup> 326–31°, <sup>595</sup> 300°, <sup>25, 386b</sup> 280–90°, <sup>427c</sup> 280°; <sup>10, 444</sup> Na salt, m. 233°. <sup>430b</sup>  
 6-Ethoxymethyl, m. 181°. <sup>363b</sup>  
 6-Diethoxymethyl, m. 160°. <sup>366b</sup>  
 6-*c*-Pentylmethyl, m. 200°. <sup>348</sup>  
 6-*c*-Hexylmethyl, m. 239°. <sup>348</sup>  
 6-(*p*-Methylphenoxyethyl), m. 300°. <sup>528</sup>  
 6-(Naphthylmethyl),  $\alpha$ -, m. 288°;  $\beta$ -, m. 268°. <sup>442</sup>  
 6-Ethyl, m. 228.5°, <sup>299</sup> 230.5°, <sup>25</sup> 227°, <sup>659</sup> 235° (dec.). <sup>430b</sup>  
 6-( $\alpha$ -Ethoxyethyl), m. 206–8°. <sup>369a</sup>  
 6-(2-*c*-Hexylethyl), m. 195°. <sup>348</sup>  
 6-(Phenylethyl),  $\alpha$ -, m. 206°;  $\beta$ -, m. 225.5°. <sup>348</sup>  
 6-Furylethyl, m. 205°. <sup>28b, 29a</sup>  
 6-Propyl, m. 219°, <sup>20a, 25, 299</sup> 215–6° (dec.), <sup>430b, 668a</sup> 217°. <sup>659</sup>  
 6-*i*-Propyl, m. 180°, <sup>25, 299</sup> 178–80°. <sup>20a</sup>  
 6-(3-*c*-Hexylpropyl), m. 183°. <sup>348</sup>  
 6-( $\alpha$ -Phenylpropyl), m. 233°. <sup>348</sup>  
 6-*n*-Butyl, m. 206°, <sup>659</sup> 207.5°, <sup>299</sup> 209°. <sup>25</sup>

- 6-*i*-Butyl, m. 220°, <sup>10</sup> 220.5°, <sup>299</sup> 221.5°. <sup>25</sup>  
 6-*s*-Butyl, m. 224°, <sup>25</sup> 222-4°. <sup>299</sup>  
 6-*t*-Butyl, m. 180°, <sup>25</sup> 178-80°. <sup>299</sup>  
 6-Amyl, m. 153-4°, <sup>299</sup> 154.5°. <sup>25</sup>  
 6-*n*-Hexyl, m. 145.5°, <sup>25</sup> 144.5°. <sup>299</sup>  
 6-Trimethylene, m. 327°. <sup>299</sup>  
 6-*c*-Propyl, m. 239°. <sup>348</sup>  
 6-*c*-Butyl, m. 212°. <sup>36c, 348</sup>  
 6-*c*-Pentyl, m. 222°, <sup>348</sup> 201-3° (dec.), <sup>36c</sup> 208° (dec.). <sup>36b</sup>  
 6-*c*-Hexyl, m. 282-285°, <sup>25, 299</sup> 238-40°. <sup>36b</sup>  
 6-Formyl, m. 250°. <sup>366b</sup>  
 6-Hydroxy, m. 235°. <sup>572</sup>  
 6-Amino, m. 295°, <sup>268</sup> 300° (cir). <sup>168</sup>  
 6-Phenyl, m. 264°, <sup>299, 659</sup> 264.5°, <sup>25</sup> 259°, <sup>371</sup> 254°. <sup>29a, 729</sup>  
 6-*p*-Chlorophenyl, m. 282°, <sup>239b</sup> 289-291°. <sup>299</sup>  
 6-Benzyl, m. 224°, <sup>299, 348</sup> 221°. <sup>659</sup>  
 6-(Methylbenzyl), *o*-, m. 206-15°, <sup>528</sup> *m*-, m. 231°; *p*-, m. 229°. <sup>528, 536</sup>  
 6-(2,4-Dimethylbenzyl), m. 262-5°. <sup>528</sup>  
 6-(Furyl), m. 286°. <sup>348</sup>  
 6-(2-Furyl), m. 298°. <sup>28c, 29a</sup>  
 6-Methylfuryl, m. 293°. <sup>29a</sup>  
 6-(Naphthyl),  $\alpha$ -, m. 307°;  $\beta$ -, m. 303°. <sup>442</sup>

### 1,5-Disubstituted

- 1-Methyl-5-hydroxy. <sup>376b</sup>  
     -5-ethoxy, m. 211°. <sup>376b</sup>  
     -5-cyano, m. 295°. <sup>43</sup>  
 1-Allyl-5-methyl, m. 234°. <sup>559</sup>  
     -5-*i*-propyl, m. 217-20°. <sup>559</sup>  
 1-Carbethoxy-5-cyano, m. 340°. <sup>43</sup>  
 1-Phenyl-5-cyano, m. 267°. <sup>43</sup>

### 1,6-Disubstituted

- 1,6-Dimethyl, m. 235-45°. <sup>427c</sup>  
 1-Methyl-6-imino. <sup>705</sup>  
 1-Allyl-6-amino, m. 230-2°. <sup>559</sup>  
 1-Phenyl-6-methyl, m. 253-5°. <sup>79</sup>  
     -6-amino, m. 240°. <sup>268</sup>

- 1-(Chlorophenyl)-6-amino, *o*-, m. 229°; *m*-, m. 219°; *p*-, m. 242°. <sup>268</sup>  
 1-(*p*-Bromophenyl)-6-amino, m. 243°. <sup>268</sup>  
 1-(Tolyl)-6-amino, *o*-, m. 227°, *p*-, m. 235°. <sup>268</sup>  
 1-(Methoxyphenyl)-6-amino, *o*-, m. 223°; *p*-, m. 213°. <sup>268</sup>

### 3,5-Disubstituted <sup>745a</sup>

- 3,5-Dimethyl, m. 230°. <sup>365a</sup>  
 3-Methyl-5-carbethoxy, m. 205°.   
 3-Ethyl-5-carbethoxy, m. 257°.   
     -5-benzoyl, m. 253°.   
 3-Methoxyethyl-5-carbethoxy, m. 202°.   
     -5-acetyl, m. 137°.   
 3-Propyl-5-carbethoxy, m. 212°.   
 3-*i*-Propyl-5-acetyl, m. 144°.   
     -5-cyano, m. 85°.   
 3-Butyl-5-carbethoxy, m. 192°.   
     -5-benzoyl, m. 183°.   
 3-*i*-Butyl-5-carbethoxy, m. 189°.   
 3-Amyl-5-carbethoxy, m. 196°.   
 3-*i*-Amyl-5-carbethoxy, m. 184°.   
 3-Hexyl-5-carbethoxy, m. 196°.   
 3-*c*-Hexyl-5-carboxy, m. 154°; Et ester, m. 194°.   
     -5-acetyl, m. 198°.   
 3-Octyl-5-carbethoxy, m. 170°.   
 3-Allyl-5-carbethoxy, m. 221°.   
 3-Phenyl-5-carboxy, m. 248°; Et ester, m. 276° (dec.).   
     -5-acetyl, m. 232°.   
 3-Benzyl-5-carbethoxy, m. 228°.

### 3,6-Disubstituted

- 3,6-Dimethyl, m. 260–5°. <sup>454</sup>  
 3-Methyl-6-benzyl, m. 222°. <sup>528</sup>  
     -6-(methylbenzyl), *m*-, m. 167°; *p*-, m. 174–6°. <sup>528, 536</sup>  
 3-Hydroxymethyl-6-methyl, m. 260° (dec.); Ac, m. 266–8° (dec.). <sup>210</sup>  
     -6-propyl, m. 130° (dec.). <sup>210</sup>  
 3-Ethyl-6-methyl, m. 203°. <sup>454</sup>  
 3-Phenyl-6-methyl, m. 266°. <sup>427b, 427c</sup> 256° (dec.). <sup>78</sup>  
     -6-carbethoxy, m. 180°. <sup>611</sup>



## 5,6-Disubstituted

- 5,6-Dimethyl, m.  $280^{\circ}$ ,<sup>146, 147c</sup>  $283-5^{\circ}$ ,<sup>299</sup>  $274^{\circ}$ ,<sup>577</sup>  $278-80^{\circ}$  (dec.).<sup>339</sup>
- 5-Methyl-6-ethyl, m.  $224^{\circ}$ ,<sup>299</sup>  $219^{\circ}$ .<sup>713</sup>
- 6-propyl, m.  $205^{\circ}$ .<sup>713</sup>
- 6-formyl, m.  $232-3^{\circ}$  (dec.).<sup>366a</sup>
- 6-[(EtO)<sub>2</sub>CH], m.  $120^{\circ}$ .<sup>366a</sup>
- 6-[NOH:CH], m.  $233^{\circ}$  (dec.).<sup>366a</sup>
- 6-[Ph·NH·N:CH], m.  $287^{\circ}$  (dec.).<sup>366a</sup>
- 6-(*p*-chlorophenyl), m.  $291^{\circ}$ .<sup>239b</sup>
- 6-[PhNH], m.  $274^{\circ}$  (dec.).<sup>366a</sup>
- 5-Hydroxymethyl-6-phenyl, m.  $251^{\circ}$ .<sup>530</sup>
- 5-Diethylaminomethyl-6-methyl, m.  $300^{\circ}$ ; HCl, m.  $211^{\circ}$ .<sup>529c</sup>
- 5-(1-Piperidylmethyl)-6-methyl, m.  $302-5^{\circ}$ ; HCl, m.  $214^{\circ}$ .<sup>529c</sup>
- 5-Ethyl-6-methyl, m.  $216-8^{\circ}$ ,  $212^{\circ}$ .<sup>361</sup>
- 6-ethyl, m.  $214.5^{\circ}$ ,  $215.5^{\circ}$ .<sup>299</sup>
- 6-phenyl, m.  $233-5^{\circ}$ .<sup>482</sup>
- 5- $\beta$ -Hydroxyethyl-6-methyl, m.  $265-7^{\circ}$ .<sup>299</sup>
- 5-(2-Ethoxyethyl)-6-methyl, m.  $203.5^{\circ}$ .<sup>701</sup>
- 5-(2-Carboxyethyl)-6-hydroxy, m.  $236^{\circ}$ .<sup>609</sup>
- 5-Propyl-6-methyl, m.  $209.5^{\circ}$ ,<sup>143</sup>  $210^{\circ}$ .<sup>147a</sup>
- 5-( $\beta$ -Chloropropyl)-6-methyl, m.  $218-20^{\circ}$  (dec.).<sup>373</sup>
- 5-Butyl-6-methyl, m.  $198^{\circ}$ .<sup>142</sup>
- 5-Amyl-6-methyl, m.  $217-9^{\circ}$ .<sup>530</sup>
- 5-Allyl-6-methyl, m.  $187^{\circ}$ .<sup>373</sup>
- 5-Hydroxy-6-Me, m.  $310^{\circ}$ .<sup>316</sup>
- 5-MeO-6-MeOCH<sub>2</sub>, m.  $188.5^{\circ}$ .<sup>316</sup>
- 5-EtO-6-EtOCH<sub>2</sub>, m.  $176^{\circ}$ .<sup>316</sup>
- 5-PrO-6-PrOCH<sub>2</sub>, m.  $137^{\circ}$ .<sup>316</sup>
- 5-*i*-PrO-6-*i*-PrOCH<sub>2</sub>, m.  $177.5^{\circ}$ .<sup>316</sup>
- 5- $\beta$ -Chloropropyl-6-methyl, m.  $220^{\circ}$ .<sup>373</sup>
- 5-BuO-6-BuOCH<sub>2</sub>, m.  $111^{\circ}$ .<sup>316</sup>
- 5-*i*-BuO-6-Me, m.  $262^{\circ}$ .<sup>316</sup>
- 6-BuOCH<sub>2</sub>, m.  $160^{\circ}$ .<sup>316</sup>
- 5-EtMeCHO-6-EtMeCHOCH<sub>2</sub>, m.  $143.5^{\circ}$ .<sup>316</sup>
- 5-Bromo-6-amino, m.  $300^{\circ}$  (cir).<sup>374b</sup>
- 5-Fluoro-6-COOH.<sup>327</sup>
- 5-Iodo-6-methyl, Na salt, m.  $233^{\circ}$  (dec.).<sup>430b</sup>
- 6-ethyl, Na salt, m.  $235^{\circ}$  (dec.).<sup>430b</sup>
- 6-propyl, Na salt, m.  $216^{\circ}$  (dec.).<sup>430b</sup>

- 5,6-Diamino,<sup>354d, 703</sup> 5-formamido.<sup>703</sup>  
 5-(*p*-Carboxyphenylamino)-6-methyl, m. 240–5°.<sup>529a</sup>  
 5-(*p*-Sulfonylphenylamino)-6-Me, m. 255–65° (dec.).<sup>529a</sup>  
 5-(2-Iodo-4-carboxyphenylamino)-6-Me, m. 230–5° (dec.).<sup>529a</sup>  
 5-(2-Iodo-4-sulfonylphenylamino)-6-Me, not melted at 310°.<sup>529a</sup>  
 5-Benzyl-6-methyl, m. 258°.<sup>528, 741a</sup>  
 5-(β-Naphthoxy)-6-naphthoxymethyl, m. 224–6°.<sup>373</sup>  
 5,6-*c*-Hexeno, m. 314–20° (dec.).<sup>184</sup>

### 1,3,6-Trisubstituted

- 1,6-Dimethyl-3-phenyl, m. 197–9°.<sup>427b</sup>  
 1,3-Diethyl-6-methyl, m. 98°.<sup>427b, 427c</sup>  
     -6-amino, m. 178–82°.<sup>560b</sup>  
 1-*i*-Propyl-3-methyl-6-amino, m. 248°.<sup>560a, 560b</sup>  
 1-Propyl-3-ethyl-6-amino.<sup>560b</sup>  
 1,3-Dipropyl-6-amino.<sup>560b</sup>  
 1,3-Di-*i*-butyl-6-amino.<sup>560b</sup>  
 1-Benzyl-3-ethyl-6-amino.<sup>560b</sup>  
 1,3-Dibenzyl-6-amino.<sup>560b</sup>

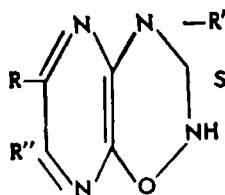
### 3,5,6-Trisubstituted

- 3,5,6-Trimethyl, m. 255°.<sup>105</sup> 256°.<sup>315</sup>  
 3,5-Dimethyl-6-amino, m. 302°.<sup>576</sup>  
 3,6-Dimethyl-5-cyano, m. 280° (dec.).<sup>745a</sup>  
 3-Ethyl-5-cyano-6-methyl, m. 268°.<sup>745a</sup>  
 3-Methoxyethyl-5-cyano-6-methyl, m. 207°.<sup>745a</sup>  
 3-Butyl-5-cyano-6-methyl, m. 234°.<sup>745a</sup>  
 3-Phenyl-5,6-dimethyl, m. 255°.<sup>315</sup>  
 3-Phenyl-5-cyano-6-ethyl, m. 263°.<sup>745a</sup>

### 1,3,5,6-Tetrasubstituted

- (4'-Phenyl-α-pyrene)-5',6',6,5-[1,3-diphenyl-2-thiouracil], m.  
 290°.<sup>611</sup>

### 2-MERCAPTOPYRIMIDO-4,5-B PYRAZINES



### 1,6,7-Trisubstituted<sup>268</sup>

R	R'	R''
Ph	Me	Me, m, 281°. <sup>270</sup>
ClC <sub>6</sub> H <sub>4</sub>	Me	Me, <i>m</i> -, m, 267°; <i>p</i> -, m, 270°.
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	Me	Me, m, 300°.
MeOC <sub>6</sub> H <sub>4</sub>	Me	Me, <i>o</i> -, m, 282–3°; <i>p</i> -, m, 280°.
<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	Me	Me, m, 292°.
Ph	Ph	Ph, m, 275°.
ClC <sub>6</sub> H <sub>4</sub>	Ph	Ph, <i>m</i> -, m, 258°; <i>p</i> -, m, 280°.
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	Ph	Ph, m, 300°.
MeOC <sub>6</sub> H <sub>4</sub>	Ph	Ph, <i>o</i> -, m, 286°; <i>p</i> -, m, 298°.
<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	Ph	Ph, m, 280°.
<i>m</i> -ClC <sub>6</sub> H <sub>4</sub>	H	H, m, 265°.
Ph	H	Ph, m, 280°.
ClC <sub>6</sub> H <sub>4</sub>	H	Ph, <i>m</i> -, m, 280°; <i>p</i> -, m, 280°.
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	H	Ph, m, 285°.
MeOC <sub>6</sub> H <sub>4</sub>	H	Ph, <i>m</i> -, m, 290°; <i>p</i> -, m, 280°.

## 4-THIOURACILS

Unsubstituted, m, 328° (dec.). <sup>738c, 740c</sup>

1-Methyl, m, 280° (dec.). <sup>301</sup>

6-Methyl, m, 250° (dec.). <sup>741a</sup>

1,3-Dimethyl, m, 280° (dec.). <sup>741a</sup>

## 2,4-DITHIOURACILS

Unsubstituted, m, 231°; <sup>412</sup> (dec.) 230°, <sup>740c</sup> 235°, <sup>734</sup> 265–70°; <sup>110a</sup> 285°. <sup>94</sup>

5-Methyl, m, 281° (dec.). <sup>741b</sup>

5-Ethoxy, m, 255° (dec.). <sup>368</sup>

5-Nitro, m, 213°. <sup>688</sup>

5-Amino, m, 270° (dec.); <sup>345</sup> 250–70°. <sup>110b</sup>

5-Benzyl, m, 262° (dec.). <sup>622</sup>

5-Phenoxy, m, 287° (dec.). <sup>622</sup>

5-(3,4-Dimethylphenoxy), m, 279° (dec.). <sup>323d</sup>

5-(*p*-Chlorophenoxy), m, 292–4°. <sup>239b</sup>

5-[(3,4-MeClC<sub>6</sub>H<sub>3</sub>)phenoxy], m, 285–7°. <sup>239b</sup>

5-[(2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)phenoxy], m, 271–5°. <sup>239b</sup>

6-Methyl, m, 240° (dec.). <sup>585b</sup> 280°. <sup>267</sup>

6-Phenyl, m, 255–9°. <sup>734</sup>

6-(2-Furyl), m, 282°. <sup>28c</sup>

1,3-Dimethyl, m, 131–3°. <sup>412</sup>

5,6-Dimethyl, m, 300° (dec.). <sup>639</sup>

- 5-Ethyl-6-methyl, darkens 250° m. 280°. <sup>119</sup>  
 5-Amino-6-methyl, m. 75°. <sup>619b</sup>  
 5-Nitro-6-methyl, m. 290° (dec.), <sup>585b</sup> 240° (dec.). <sup>585a</sup>  
 1,3-Diphenyl-6-ethoxy, m. 250°. <sup>745b</sup>

### 2-THIOCYSTOSINE AND DERIVATIVES <sup>745a</sup>

- Unsubstituted (2-Mercapto-4-aminopyrimidine), m. 265°, 273°. <sup>110a</sup>  
 5-Carbethoxy (2-Mercapto-4-NH<sub>2</sub>-5-COOEt-pyrimidine), m. 273°. <sup>110a</sup>  
 3-Methyl-5-carbethoxy, m. 238° (dec.).  
 3-Ethyl-5-carbethoxy, m. 252°. <sup>110a</sup>  
 3-Methoxyethyl-5-carbethoxy, m. 206°. <sup>110a</sup>  
     -5-cyano, m. 198°. <sup>110a</sup>  
 3-*i*-Propyl-5-cyano, m. 178°. <sup>110a</sup>  
 3-*n*-Butyl-5-carbethoxy, m. 249°. <sup>110a</sup>  
     -5-cyano, m. 228°. <sup>110a</sup>  
 3-*i*-Butyl-5-carbethoxy, m. 235°. <sup>110a</sup>  
     -5-cyano, m. 242°. <sup>110a</sup>  
 3-*n*-Amyl-5-carbethoxy, m. 228°. <sup>110a</sup>  
 3-*i*-Amyl-5-carbethoxy, m. 252°. <sup>110a</sup>  
 3-Hexyl-5-carbethoxy, m. 240°. <sup>110a</sup>  
 3-*c*-Hexyl-5-carbethoxy, m. 250°. <sup>110a</sup>  
 3-Octyl-5-carbethoxy, m. 243°. <sup>110a</sup>  
     -5-cyano, m. 225°. <sup>110a</sup>  
 3-Phenyl-5-carbethoxy, m. 251°. <sup>110a</sup>  
     -5-cyano, m. 242°. <sup>110a</sup>  
 3-Benzyl-5-carbethoxy, m. 241°. <sup>110a</sup>  
 3-Methoxyethyl-5-cyano-6-methyl, m. 233°. <sup>110a</sup>  
     -6-ethyl, m. 202°. <sup>110a</sup>  
 3-Butyl-5-cyano-6-methyl, m. 256°. <sup>110a</sup>  
 3-*i*-Propyl-5-cyano-6-ethyl, m. 254°. <sup>110a</sup>  
 3-Octyl-5-cyano-6-ethyl, m. 245°. <sup>110a</sup>  
 3-*c*-Hexyl-5-cyano-6-methyl, m. 270°. <sup>110a</sup>

### ADDITIONAL THIOBARBITURIC ACIDS

(See Volume V, Chapter 4)

- Unsubstituted, m. 325° (dec.). <sup>90, 346</sup>  
 2-Methylmercaptobarbituric acid, m. 300°. <sup>736</sup>

5-Oximino, m. 300°. <sup>384</sup>

1,3-Diphenyl, m. 244°. <sup>346</sup>

1,3-Diphenyl-5-*i*-propyl, m. 237–40°. <sup>746</sup>

-5-benzyl, m. 254° (dec.). <sup>746</sup>

-5-(2-nitrobenzyl), m. 236° (dec.). <sup>746</sup>

-5-PhCH:CHCH, m. 278° (dec.). <sup>746</sup>

-5-oximino, m. 224°, <sup>90</sup> 212°. <sup>746</sup>

-5-phenylhydrazone, m. 291°. <sup>746</sup>

-5-(4-nitrophenylhydrazone), m. 288°. <sup>746</sup>

-5-bromo, m. 220°. <sup>47</sup>

### SULFIDES

2-[2-Thio-6-oxypyrimidyl-(5)]-thio-4-pyrimidone, m. 285–95°. <sup>386a</sup>

-thio-6-Me-4-pyrimidone, m. 300°. <sup>386a</sup>

6,6'-*bis*-(2-NH<sub>2</sub>-4-Me-pyrimidyl) sulfide, m. 224°; sulfone, m. 220°. <sup>585a</sup>

6,6'-*bis*-(2,4-Dimethylpyrimidyl) sulfide, m. 77–9°. <sup>551</sup>

### DISULFIDES

*bis*-[5-Ethoxy-pyrimidyl-(2)]-, m. 125°. <sup>377a</sup>

*bis*-[4,6-Dimethyl-pyrimidyl-(2)]-, m. 163°. <sup>628</sup>

*bis*-[2,6-Dimethyl-pyrimidyl-(4)]-, m. 99°. <sup>267</sup>

*bis*-[2,4-Dihydroxy-6-amino-pyrimidyl-(5)]-, m. 360°. <sup>61a</sup>  
-6-methyl-pyrimidyl-(5)]-, m. 334° (dec.). <sup>468</sup>

*bis*-[1-Methyl-2,4-dioxo-6-imino-hexahydropyrimidyl-(5)]-, m. 350°. <sup>61b</sup>

*bis*-[2-Amino-4-hydroxy-6-methyl-pyrimidyl-(5)]-, m. 300°. <sup>468</sup>

*bis*-[2-Amino-4-hydroxy-6-phenyl-pyrimidyl-(5)]-, m. 300°. <sup>369</sup>

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## CHAPTER 3

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# Organic Sulfur-Fluorine Compounds

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by

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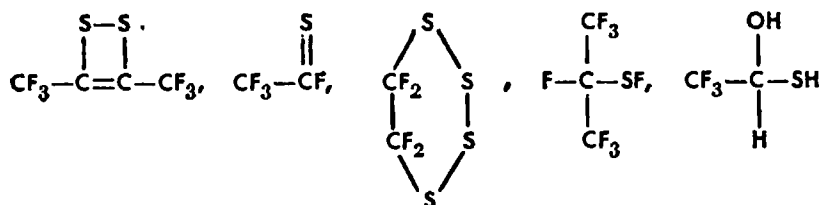
### General

The complete substitution of fluorine for hydrogen has a marked effect on both the chemical and physical properties of organic compounds of bivalent sulfur. Because of the strongly electron-withdrawing character of fluorine in these compounds, the sulfur atom is relatively electron-poor. Consequently, such compounds are generally more resistant to electrophilic reagents, but more reactive toward nucleophilic reagents than their unfluorinated analogs.

In addition to the changes in chemical reactivity, the thermal stability of organic compounds of bivalent sulfur is often greatly altered by the substitution of fluorine. The presence of fluorine may either stabilize or destabilize such compounds in comparison to their fluorine-free analogs. In general, the highly fluorinated

compounds are considerably more stable than the corresponding fluorine-free derivatives. This is due, at least in part, to the strengthening of the C—S bonds by the electron-withdrawing fluorine atoms. In a few cases, however, the perfluoro compounds are less stable. This is true of the  $\alpha$ -fluoroalkylthiols, because these compounds lose the elements of hydrogen fluoride easily to given thiocarbonyl compounds.

Several perfluoro compounds have been prepared for which the unfluorinated analogs are unknown, such as the following:



### PHYSICAL PROPERTIES

Many fluorine-containing compounds of bivalent sulfur have been prepared. A number of these are listed in the tables at the end of the chapter. It will be noted that complete substitution of fluorine for hydrogen lowers the boiling point when compared to the corresponding unfluorinated analog. This is most noticeable in the compounds of lower molecular weight, as seen in Table 3.1.

Partial substitution of fluorine appears to have an unpredictable effect. In instances where hydrogen-bonding is important, the partially substituted compounds generally have higher boiling points than either the perfluoro or the fluorine-free compound. Table 3.2 illustrates this effect with ethanethiol.

When effects due to hydrogen-bonding are slight, the boiling points are often lowered progressively by introduction of fluorine atoms, as shown in Table 3.3 for the methyl sulfides.

As is the case with most fluorine-containing compounds, the sulfur-fluorine compounds have lower indexes of refraction and higher density than the corresponding compounds containing hydrogen in place of fluorine.

### Fluorothiols

Only a few aliphatic thiols containing  $\alpha$ -fluorine atoms are known. Of these, only  $\text{CF}_3\text{SH}^{44}$  appears to be stable indefinitely



TABLE 3.1

Compound	Boiling Point	Perfluoro Analog	Boiling Point
$\text{CH}_3\text{SH}$	7°	$\text{CF}_3\text{SH}$	-36.7°
$\text{CH}_3\text{SCH}_3$	38°	$\text{CF}_3\text{SCF}_3$	-22°
$\text{CH}_3\text{SCI}$	91-94° (extrapolated)	$\text{CF}_3\text{SCI}$	-1°
$\text{CH}_3-\overset{\text{O}}{\parallel}\text{CSH}$	88°	$\text{CF}_3-\overset{\text{O}}{\parallel}\text{CSH}$	35.5°
$\text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\text{SCH}_3$	98°	$\text{CF}_3-\overset{\text{O}}{\parallel}\text{C}-\text{SCF}_3$	24°
$\text{CH}_3\text{SSCH}_3$	116°	$\text{CF}_3\text{SSCF}_3$	34°
$\begin{array}{c} \text{CH}_3-\text{CH}_3 \\   \quad   \\ \text{CH}_2 \quad \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{S} \end{array}$	121°	$\begin{array}{c} \text{CF}_2-\text{CF}_2 \\   \quad   \\ \text{CF}_2 \quad \text{CF}_2 \\ \diagdown \quad \diagup \\ \text{S} \end{array}$	42.3°
$\begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ (\text{CH}_3)_2\text{C} \quad \text{C}(\text{CH}_3)_2 \\ \diagdown \quad \diagup \\ \text{S} \end{array}$	183.5°	$\begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ (\text{CF}_3)_2\text{C} \quad \text{C}(\text{CF}_3)_2 \\ \diagdown \quad \diagup \\ \text{S} \end{array}$	110°

TABLE 3.2

*Ethanethiols*

Fluorine Content	Compound	Boiling Point
F <sub>0</sub>	$\text{CH}_3\text{CH}_2\text{SH}$	6°
F <sub>1</sub>	$\text{CH}_2\text{FCH}_2\text{SH}$	70° (extrapolated)
F <sub>2</sub>	$\text{CHF}_2\text{CH}_2\text{SH}$	64°
F <sub>3</sub>	$\text{CF}_3\text{CH}_2\text{SH}$	34-5° (36.5°)
F <sub>3</sub>	$\text{CHF}_2\text{CHF}_2\text{SH}$	70° (extrapolated)
F <sub>4</sub>	$\text{CHF}_2\text{CF}_2\text{SH}$	25-7° (31°)
F <sub>5</sub>	$\text{CF}_3\text{CF}_2\text{SH}$	-6°

TABLE 3.3

*Methyl Sulfides*

Fluorine Content	Compound	Boiling Point
0	$\text{CH}_3\text{SCH}_3$	38°
3	$\text{CF}_3\text{SCH}_3$	12°
5	$\text{CHF}_2\text{SCF}_3$	1°
6	$\text{CF}_3\text{SCF}_3$	-22°

at room temperature. The other  $\alpha$ -fluorothiols, such as perfluoropropanethiol and tetrafluoroethanethiol can be kept at  $-20^\circ$  for several weeks, but after a day at room temperature, much decomposition occurs.<sup>43</sup> All of the  $\alpha$ -fluorothiols will lose the elements of HF when treated with sodium fluoride or other basic reagents, giving thiocarbonyl compounds;<sup>85, 43, 47, 54, 77, 86</sup> and they are easily hydrolyzed with water to give thiolacids.<sup>33, 34, 35</sup>

In contrast to the  $\alpha$ -fluorothiols, the fluoroaliphatic thiols that contain no  $\alpha$ -fluorine atoms are quite stable. As would be expected, they are considerably more acidic than their nonfluorinated analogs.<sup>41</sup> For example, the  $pK_a$  of the primary thiol, 1,1-dihydroperfluoro-1-butanethiol, is 8.3, whereas that of 1-butanethiol is 12.4 in 50% aqueous ethanol. The  $pK_a$  of 3-monohydroperfluoro-3-pentanethiol is 4.6, indicating that this secondary thiol is even more acidic. The enhanced acidity of these fluorinated thiols can be explained on the basis of the highly electronegative character of the fluoroalkyl groups, and it is consistent with the increased acidities reported for fluorinated alcohols and carboxylic acids.

The infrared spectra of fluorinated thiols show the expected shift of the SH stretching band to higher wave numbers (shorter wave length) as a result of the inductive effect of the fluorine atoms. Trifluoromethanethiol absorbs at  $2618\text{ cm}^{-1}$ ,<sup>18</sup>  $\text{CHF}_2\text{-CF}_2\text{SH}$  at  $2608\text{ cm}^{-1}$ , and  $\text{CHClFCF}_2\text{SH}$  at  $2612\text{ cm}^{-1}$ .<sup>34</sup> Even the thiols that contain  $\beta$ -fluorines but no  $\alpha$ -fluorines show absorption in the region of  $2590\text{--}2600\text{ cm}^{-1}$ ,<sup>41</sup> indicating a distinct shift from the absorption around  $2575\text{ cm}^{-1}$  of their unfluorinated analogs. In addition to the shift in position, the absorption band for SH is considerably more intense for the fluorinated thiols.<sup>41</sup>

A few fluorine-containing aromatic thiols are known. Perfluorobenzenethiol<sup>110</sup> appears to be susceptible to nucleophilic attack, as are most other highly-fluorinated aromatic compounds. Perfluorobenzenethiol is easily desulfurized with Raney nickel, giving pentafluorobenzene.<sup>123</sup> Other aromatic thiols that contain less fluorine appear to be more stable chemically.<sup>100, 101, 120</sup>

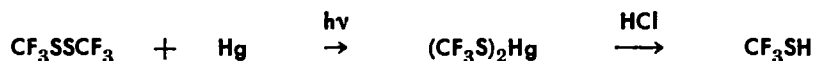
Except for the  $\alpha$ -fluorothiols, most of the fluorine-containing thiols appear to behave chemically very much like their unfluorinated analogs. For example, they can be oxidised to disulfides<sup>41, 101, 110</sup> and sulfonic acids,<sup>41</sup> and chlorinated to sulfenyl chlorides.<sup>39, 41, 43</sup> They form fluoroalkyl-2,4-dinitrophenyl sulfides with 2,4-

dinitrochlorobenzene,<sup>41</sup> and they undergo free radical addition to olefins.<sup>43</sup> The  $\alpha$ -fluorothiols, in addition to undergoing some of these reactions, also lose hydrogen fluoride easily. These reactions will be discussed later in connection with the preparation of fluorine-containing thiocarbonyl compounds.

## PREPARATION

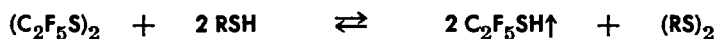
### *Reduction of Disulfides*

Most of the known perfluoroalkyl thiols have been prepared by reduction of the corresponding disulfides. Irradiation of a mixture of  $\text{CF}_3\text{SSCF}_3$  and mercury with ultraviolet light gives the mercuric salt of  $\text{CF}_3\text{SH}$ .<sup>5, 44</sup> The free mercaptan is liberated by treating the salt with anhydrous hydrogen chloride.



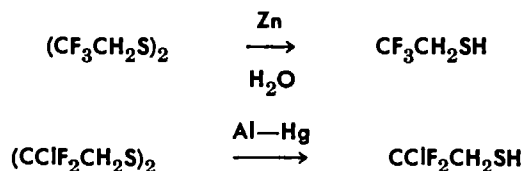
Perfluoropropanethiol has been prepared in a similar manner from perfluoropropyl disulfide and mercury.<sup>47</sup>

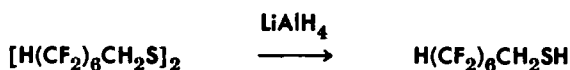
Another very similar method has been used to prepare perfluoroalkyl thiols, using a higher-boiling thiol instead of mercury as the reducing agent. For example, perfluoroethanethiol is prepared by irradiating a mixture of  $\text{H}(\text{CF}_2)_2\text{CH}_2\text{SH}$  and  $(\text{C}_2\text{F}_5\text{S})_2$  with ultraviolet light.<sup>86, 95</sup> An equilibrium mixture containing both disulfides and thiols is formed, and the most volatile component of the mixture,  $\text{C}_2\text{F}_5\text{SH}$ , is removed preferentially by distillation.



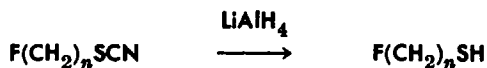
Other perhalothiols, including  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SH}$ ,<sup>86</sup>  $\text{C}_2\text{F}_5\text{CFSHCF}_3$ ,<sup>54</sup> and  $\text{CClF}_2\text{CF}_2\text{SH}$ <sup>86, 95</sup> have been prepared by this method.

More conventional chemical reductions can be used to prepare thiols that have no  $\alpha$ -fluorines. 2,2,2-Trifluoroethyl disulfide is reduced by zinc and water,<sup>1, 5</sup> and 2-chloro-2,2-difluoroethyl disulfide is reduced by aluminum amalgam.<sup>61</sup> Lithium aluminum hydride has also been used to effect similar reductions.<sup>31</sup>



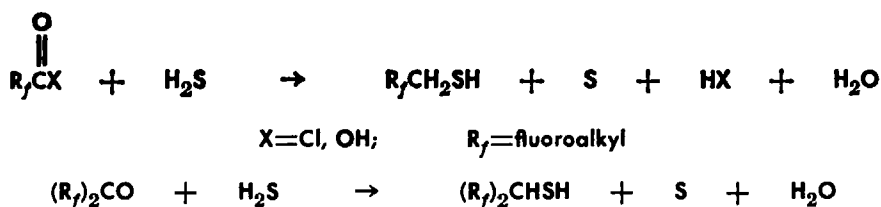


Lithium aluminum hydride has been used to prepare a series of  $\omega$ -fluoromercaptans from the corresponding thiocyanates.<sup>55</sup>



### *Reductive Thiolation of Carbonyl Compounds*

The reductive thiolation of fluorinated acids, acid chlorides, ketones, and aldehydes provides a convenient route to a variety of highly fluorinated thiols.<sup>41</sup> The uncatalyzed reaction of perfluorocarboxylic acids or their acid chlorides with hydrogen sulfide at 200–250° and pressures of 2000–3000 atmospheres gives  $\alpha,\alpha$ -dihydroperfluorothiols in yields that range from 20–60%. Fluoroketones are reduced under similar conditions to give secondary thiols.



Autogeneous pressure is sufficient to convert fluorinated aldehydes or their hydrates to thiols.<sup>41</sup>



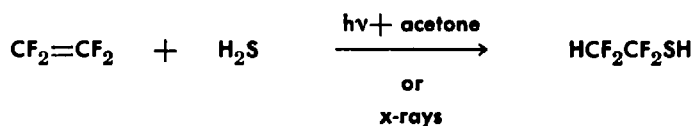
In some of these reactions, the corresponding di- and trisulfides are obtained as by-products.

It is interesting to note that the fluorinated carbonyl compounds undergo reductive thiolation much more readily than their hydrocarbon counterparts.<sup>41</sup>

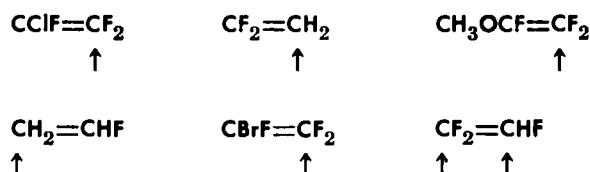
### *Addition of Hydrogen Sulfide to Fluoroölefins*

Free radical addition of hydrogen sulfide to fluoroölefins appears to be a general method for the preparation of highly fluorinated thiols. Hydrogen sulfide adds smoothly to such fluoroölefins as tetrafluoroethylene,<sup>34, 43</sup> difluoroethylene,<sup>35</sup> chloro-<sup>34, 43</sup>

and bromotrifluoroethylenes,<sup>43</sup> and hexafluoropropylene<sup>35</sup> under the influence of x-rays or ultraviolet light.



The unsymmetrical fluoroolefins could add hydrogen sulfide in either of two ways and give two possible products. The resulting orientation can most generally be explained by assuming that the  $\text{HS}\cdot$  radical adds to give the more stable of the two possible intermediate radicals, and the predominate or exclusive product results from chain transfer by this addition compound with  $\text{H}_2\text{S}$ .<sup>43</sup> For example, the adding  $\text{HS}\cdot$  radical attacks the carbon indicated by the arrows in the following formulas, giving the corresponding thiols:



In the reaction with trifluoroethylene, both isomers are obtained, indicating attack by the  $\text{HS}\cdot$  radical at both the CHF and the  $\text{CF}_2$  groups of the olefin, with the major attack occurring at the CHF group.

Both isomers are also obtained when the addition of  $\text{H}_2\text{S}$  to vinylidene fluoride and hexafluoropropylene is induced by ultraviolet light.<sup>35</sup>

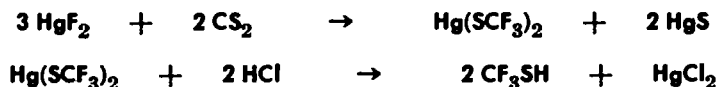


In additions induced by both x-ray and ultraviolet light, sulfides are obtained as by-products. The G values for the x-ray-induced experiments indicate that the kinetic chain length is unusually large.<sup>43</sup>

#### *From Thiocarbonyl Compounds*

The most convenient method for the preparation of  $\text{CF}_3\text{SH}$  appears to be the reaction of metal fluorides with carbon disulfide. The mercuric salt of this thiol is formed in 72% yield from the

reaction of mercuric fluoride with excess carbon disulfide at 250°. <sup>98</sup> Silver fluoride will also fluorinate carbon disulfide, giving the silver salt of trifluoromethanethiol. <sup>27</sup> The free thiol can be generated from these salts by treating them with dry hydrogen chloride.



A somewhat related reaction is the addition of mercuric fluoride to thiocarbonyl fluoride. <sup>20</sup>

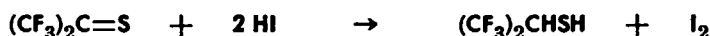


Several other salts of  $\text{CF}_3\text{SH}$  have been prepared by exchange reactions of  $\text{Hg(SCF}_3)_2$  with other salts of mercury. Examples include  $\text{CF}_3\text{SHgX}$ , where X is Cl, Br, I, CN, <sup>21</sup> OAc,  $\text{NO}_3$ , and  $\text{CF}_3\text{CO}$ . <sup>22</sup>



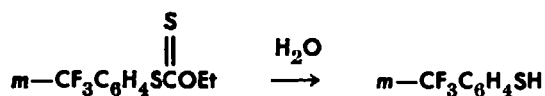
The mercury salt of  $\text{CF}_3\text{SH}$  also reacts with copper to give the cuprous salt, and with silver nitrate to give the silver salt. <sup>98</sup>

Thiocarbonyl compounds can be reduced to give thiols. Reduction of hexafluorothioacetone with anhydrous hydrogen iodide gives the corresponding thiol in high yield. <sup>96</sup>



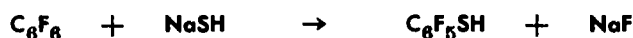
#### *Hydrolysis of Thioesters*

Both aliphatic and aromatic fluorine-containing thiols have been prepared by hydrolysis of thiolesters. Treatment of  $\text{AcSCH}_2\text{CH}_2\text{F}$  with anhydrous hydrogen chloride at 60° gives a 74% yield of  $\text{FCH}_2\text{CH}_2\text{SH}$ . <sup>25</sup> The three isomeric fluorothiophenols <sup>101</sup> as well as *m*-trifluoromethylthiophenol have been prepared by hydrolysis of the corresponding xanthates synthesized from the fluorine-containing anilines.



#### *Nucleophilic Displacement of Halide*

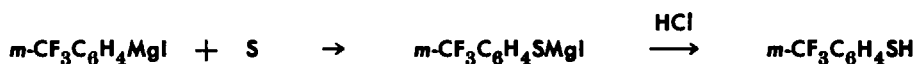
Perfluorobenzene reacts with NaSH in boiling pyridine to give perfluorothiophenol. <sup>110</sup>



2,3,5,6-Tetrafluorobenzenethiol<sup>110</sup> and trifluoromethyl-4-nitrobenzenethiol<sup>9, 101</sup> are prepared in a similar manner from pentafluorobenzene and 2-chloro-5-nitrobenzotrifluoride, respectively. Reaction of  $\text{FCH}_2\text{CH}_2\text{Br}$  with  $\text{NaSH}$  gives  $\text{FCH}_2\text{CH}_2\text{SH}$ .<sup>83</sup>

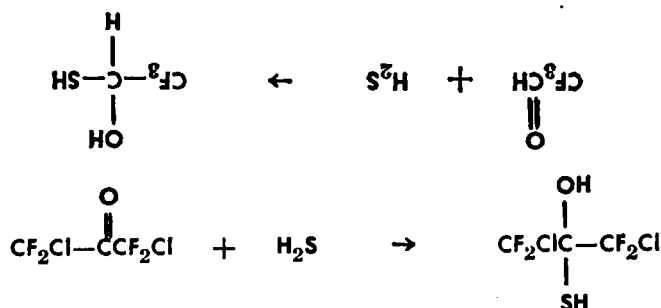
### Miscellaneous

Reduction of  $p\text{-FC}_6\text{H}_4\text{SO}_2\text{OCH}_2\text{CH}_2\text{F}$  with zinc gives good yields of  $p$ -fluorothiophenol.<sup>100</sup>  $m$ -Trifluoromethylbenzenethiol is obtained by treating  $m$ -trifluoromethylphenylmagnesium bromide with sulfur.<sup>122</sup>



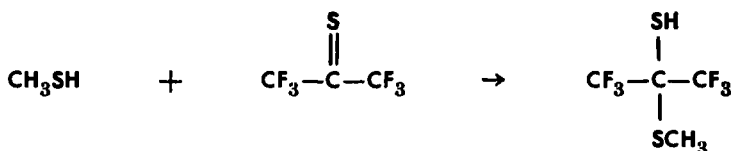
### $\alpha$ -SUBSTITUTED THIOLS

Hydrogen sulfide adds to highly fluorinated aldehydes and ketones at  $80^\circ$  to give olthiols that can be distilled *in vacuo*.<sup>38</sup>



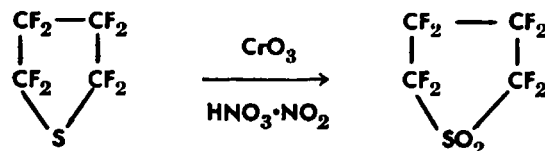
There is a considerable variation in stability within this group of compounds. The olthiol derived from  $s$ -dichlorotetrafluoroacetone is stable for several days at room temperature, while the olthiol derived from decafluoro-3-pentanone is completely decomposed after a few hours at room temperature. The corresponding unfluorinated analogs of these olthiols are too unstable for isolation.

Highly fluorinated hemidithioketals are also relatively stable. Methyl and ethyl mercaptan add to hexafluorothioacetone, giving the corresponding hemidithioketals as the major product.<sup>96</sup>



### Sulfides

Fluoroalkyl sulfides are considerably more inert than the corresponding fluorine-free sulfides. They do not add bromine or form adducts with salts of heavy metals, and they do not form sulfonium salts with methyl iodide as do ordinary alkyl sulfides.<sup>107</sup> Perfluoroalkyl sulfides are oxidised only with very strong oxidising agents, such as a boiling solution of chromium trioxide in fuming nitric acid:<sup>11</sup>



Milder oxidants, such as hydrogen peroxide, are ineffective.<sup>92</sup> Although the perfluoroalkyl disulfides react with alcoholic or aqueous base, the simple perfluoroalkyl sulfides do not.<sup>5, 92</sup> The aromatic ring of trifluoromethyl phenyl sulfide can be brominated and nitrated, and the nitro derivative can be reduced, diazotized, etc., without affecting the sulfide linkage.<sup>134</sup>

Examination of the nuclear magnetic resonance spectra of aromatic rings substituted with  $\text{SCF}_3$  groups indicates that this group is electron-accepting, its ability falling between  $\text{CF}_3$  and  $\text{OCF}_3$ .<sup>8</sup> The magnetic shielding of  $\text{F}^{19}$  in  $\text{SCF}_3$ , however, is less than either of these two groups.

### PREPARATION

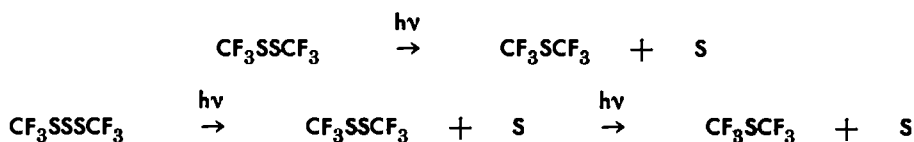
#### *From Fluoroalkyl Iodides with Sulfur*

Perfluoroalkyl sulfides have been prepared by heating a perfluoroalkyl iodide with sulfur. This procedure, however, generally results in a mixture of mono-, di-, and polysulfides, with the monosulfide being the minor product. Only a small yield of  $(n\text{-C}_3\text{F}_7)_2\text{S}$  is obtained when  $n\text{-C}_3\text{F}_7\text{I}$  is heated with sulfur at  $250^\circ$ .<sup>50, 62</sup> A larger yield (11%) is obtained when the same two reactants are heated at  $300^\circ$ .<sup>125</sup> Perfluoroisopropyl sulfide, in mixture with the di- and trisulfides, is similarly prepared in 11% yield from perfluoroisopropyl iodide and sulfur at  $243^\circ$ ,<sup>14</sup> and  $[\text{H}(\text{CF}_2)_6\text{CH}_2]_2\text{S}$  is formed from  $\text{H}(\text{CF}_2)_6\text{CH}_2\text{I}$  and sulfur at  $250\text{--}270^\circ$ .<sup>31</sup>

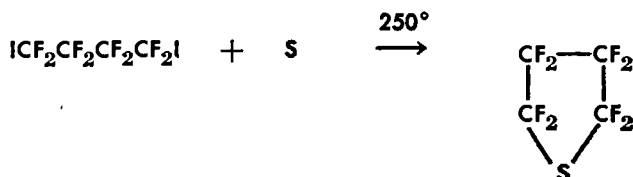
*Bis*-(trifluoromethyl)sulfide is obtained in poor yield from



$\text{CF}_3\text{I}$  and sulfur, the predominant product being the di- and tri-sulfide. The monosulfide can be obtained from these higher sulfides, however, by photochemical decomposition.<sup>5, 44</sup>

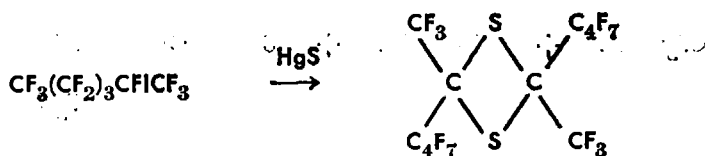


The perfluorodiiiodide,  $\text{ICF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ , reacts with sulfur to give exclusively the monosulfide, octafluorothiolane.<sup>124</sup>



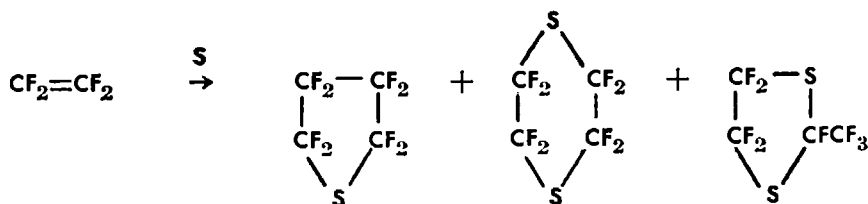
A free radical mechanism has been postulated to account for the formation of sulfides by reaction of fluoroalkyl iodides with sulfur.<sup>5</sup>

A somewhat related reaction is the formation of a dithietane from 2-iodoperfluorohexane—or the corresponding disulfide—and black mercuric sulfide at  $225^\circ$ .<sup>48</sup>



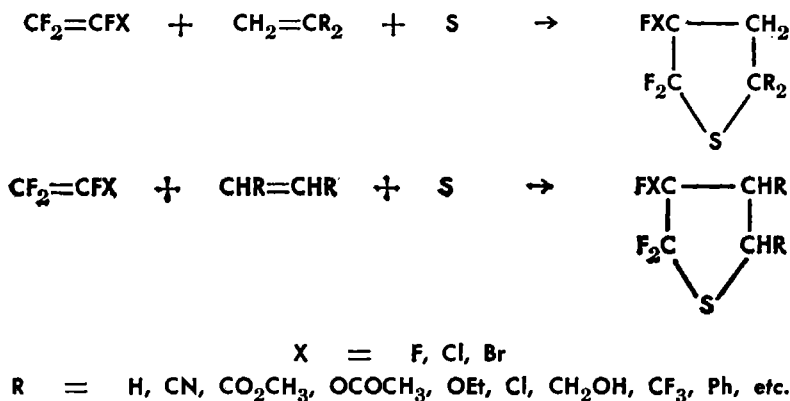
#### *From Fluoroolefins with Sulfur*

A number of fluorinated cyclic sulfides have been obtained by the direct reaction of fluoroolefins with sulfur. Octafluorothiolane and octafluoro-1,4-dithiane are prepared in 15% and 60% yields, respectively, from the action of sulfur on tetrafluoroethylene at  $250\text{--}300^\circ$ .<sup>63, 70</sup> 2-Trifluoromethylpentafluoro-1,3-dithiolane is also obtained as a by-product. Iodine can be used as a coreactant with tetrafluoroethylene and sulfur to prevent the possibility of polymerization.

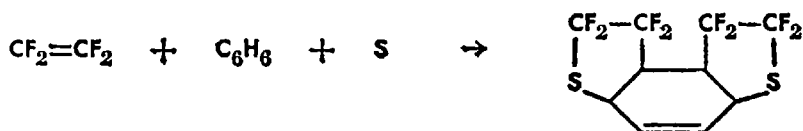


Hexafluoropropylene reacts with sulfur at 300° to give a product to which was first assigned a 1,4-dithiane structure.<sup>6</sup> This same product is obtained from the pyrolysis of sodium perfluorobutyrate in the presence of sulfur.<sup>6</sup> This product has now been identified as 2,2,4-tris-(trifluoromethyl)-trifluoro-1,3-dithiolane on the basis of NMR data.<sup>70</sup>

The one-step synthesis of octafluorothiolane from sulfur and tetrafluoroethylene has been modified by the addition of an unsaturated third component to give partially fluorinated thiolanes.<sup>65, 68</sup> Equimolar amounts of sulfur, tetrafluoroethylene, and another unsaturated component combine at 150° in a remarkably specific reaction to form, in yields up to 60%, a thiolane containing one unit of each reactant. The third component can contain terminal or internal unsaturation, and functional groups such as ester, anhydride, nitrile, hydroxyl, ether, sulfide, or halide will survive the reaction. Furthermore, chloro- and bromotrifluoroethylene can be substituted for tetrafluoroethylene.



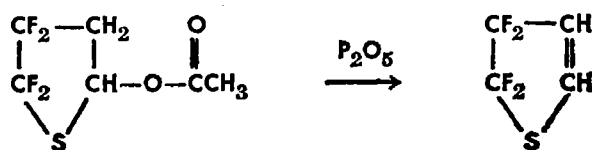
The third component in this reaction can also be an aromatic compound such as benzene or thiophene, in which case polycyclic sulfides are obtained.



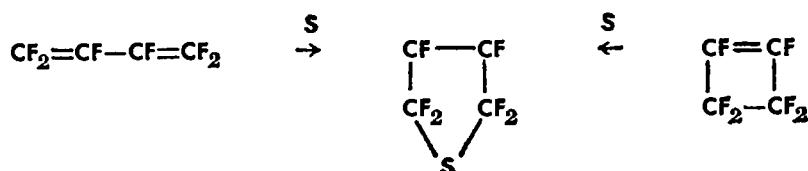
Radical mechanisms have been proposed for these syntheses of thiolanes.<sup>68</sup>

Pyrolysis over P<sub>2</sub>O<sub>5</sub> of the thiolane prepared from tetrafluoro-

ethylene, vinyl acetate and sulfur gives 2,2,3,3-tetrafluoro-2,3-dihydrothiophene.<sup>68</sup>



Unsaturated perfluorocyclic sulfides are prepared from the interaction of certain unsaturated fluorocarbons with sulfur. Perfluorobutadiene reacts with sulfur at 300° to give a perfluoro-dihydrothiophene.<sup>3</sup> This same compound is also prepared from hexafluorocyclobutene and sulfur at 300°.<sup>66</sup>

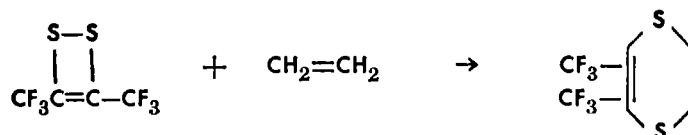


Perfluorobutyne-2 reacts with sulfur to give, among other products, *tetrakis*-(trifluoromethyl)thiophene.<sup>64</sup>

Numerous thiocarbonyl and cyclic disulfide and polysulfide compounds have also been prepared by the action of elemental sulfur on unsaturated fluorocarbons. These reactions will be discussed later in this chapter.

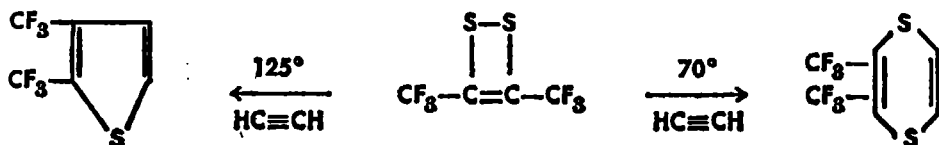
### Additions of Disulfides to Olefins

The radical-catalyzed thermal addition of dimethyl disulfide to tetrafluoroethylene to give liquid telemers, including  $\text{CH}_3\text{S}-(\text{CF}_2\text{CF}_2)_{10}\text{SCH}_3$ , has been patented.<sup>37</sup> The cyclic disulfide, *bis*-(trifluoromethyl)-1,2-dithietene, adds smoothly at 150° to a wide variety of unsaturated compounds, including ethylene, tetramethylethylene, vinyl ethers and sulfides, and other electron-rich olefins to give dihydrothiins.<sup>71, 72</sup>



The dithietene also adds to acetylenes, but because of the instability of the *p*-dithiin ring at elevated temperatures, sulfur is sometimes eliminated, giving a thiophene. With acetylene itself,

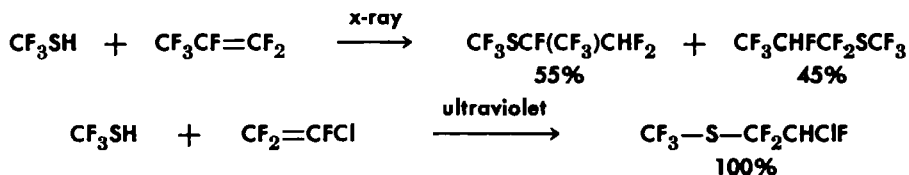
either the dithiin or the thiophene can be isolated, depending upon the temperature of reaction.



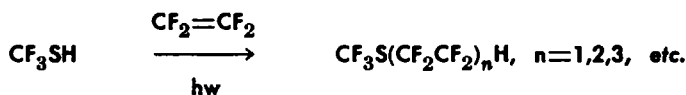
### Addition of Thiols to Olefins

The addition of thiols to olefins provides a versatile method for preparing fluorine-containing sulfides. Both radical and ionic additions have been investigated.

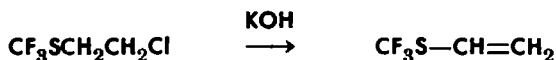
The addition of  $\text{CF}_3\text{SH}$  to tetrafluoroethylene and a number of other olefins proceeds smoothly under the influence of irradiation by ultraviolet or x-ray.<sup>42</sup> With hexafluoropropylene and trifluoroethylene, both possible 1:1 adducts are obtained. In the other olefins, the direction of addition of the  $\text{CF}_3\text{S}\cdot$  radical can be predicted by assuming that the more stable intermediate radical would be formed.



In some cases, it is possible to prepare higher adducts or telemers by this reaction. For example,  $\text{CF}_3\text{SH}$  can be added to tetrafluoroethylene to give products containing several units of tetrafluoroethylene.<sup>42</sup>



The adduct of  $\text{CF}_3\text{SH}$  with vinyl chloride can be dehydrochlorinated with refluxing alcoholic potassium hydroxide to give a vinyl sulfide.<sup>42</sup> This sulfide and other similar perfluoroalkyl vinyl sulfides can be homopolymerized and copolymerized with acrylonitrile and methyl methacrylate.



Under the influence of x-rays<sup>43</sup> or ultraviolet radiation,<sup>34</sup> hydrogen sulfide also adds to fluoroölefins, giving both sulfides and disulfides in addition to the thiols that are the principal products. Unsymmetrical fluorinated disulfides have been prepared by first adding the hydrogen sulfide to one fluoroölefin, and then adding the resulting thiol to a different fluoroölefin.<sup>43</sup>



Other reported free radical additions to fluoroölefins include the addition of thiophenol to perfluoro-1,5-hexadiene induced by benzoyl peroxide;<sup>97</sup> and the addition of ethanethiol to tetrafluoroethylene with the same initiator.<sup>37</sup>

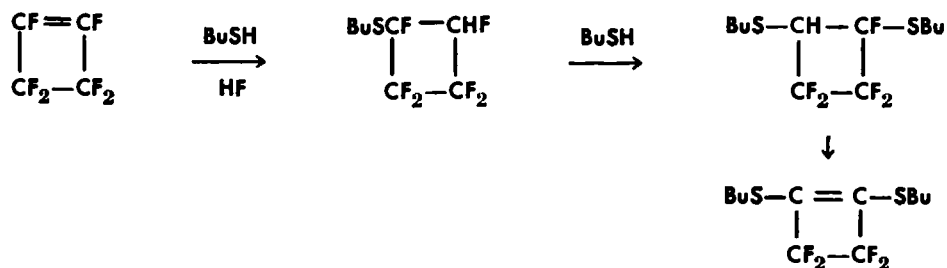
A number of base-catalyzed additions of thiols to fluoroölefins have been reported.<sup>30, 58, 60, 97, 108</sup> Methyl-, ethyl-, and isopropyl-mercaptan, as well as thiophenol, add to  $\text{CF}_2=\text{CF}_2$ ,  $\text{CFCl}=\text{CF}_2$ , and  $\text{CFCl}=\text{CFCl}$  at  $115^\circ$  in an autoclave using sodium hydroxide as a catalyst.<sup>58</sup> Sodium hydroxide has also been used to catalyze the addition of various mercaptans to hexafluoropropylene to give products of the type  $\text{CF}_3\text{CHFCH}_2\text{SR}$ .<sup>60</sup>

In these base-catalyzed reactions, the mercaptans apparently add to hexafluoropropylene exclusively in one direction. This can be contrasted with the previously mentioned radical-catalyzed additions of mercaptans to hexafluoropropylene, which give products derived from both directions of addition.

"Triton B" (benzyltrimethylammonium hydroxide) is reported to be a better catalyst than sodium hydroxide for these additions.<sup>106</sup> This catalyst has been used to add thiols to fluoroölefins such as perfluorocyclobutene,  $\text{CF}_2=\text{CCl}_2$ ,  $\text{CFCl}=\text{CF}_2$ ,<sup>106</sup> and  $\text{CF}_2=\text{CF}_2$ .<sup>30</sup> Some of these additions occur at temperatures as low as  $25^\circ$ . The addition of  $\text{HOCH}_2\text{CH}_2\text{SH}$  to  $\text{CF}_2=\text{CFCl}$  to give  $\text{HOCH}_2\text{CH}_2\text{SCF}_2\text{CHClF}$ ,<sup>106</sup> and the addition of  $o\text{-NH}_2\text{C}_6\text{H}_4\text{SH}$  to tetrafluoroethylene to give  $o\text{-NH}_2\text{C}_6\text{H}_4\text{SCF}_2\text{CF}_2\text{H}$ <sup>30</sup> under the influence of basic catalyst, indicates that the SH groups rather than the OH or  $\text{NH}_2$  groups add preferentially to the fluoroölefins.

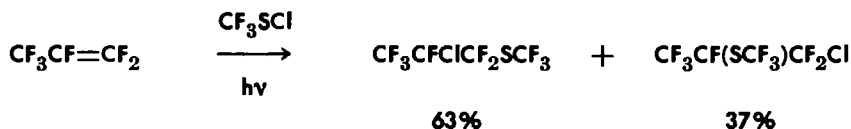
Loss of HF can occur in some cases when thiols are added to fluoroölefins in the presence of base. The unsaturated sulfide,  $\text{C}_{12}\text{H}_{25}\text{S}-\text{CF}=\text{CFCF}_3$ , is formed by the reaction of  $\text{C}_{12}\text{H}_{25}\text{SH}$  with hexafluoropropylene in the presence of potassium car-

bonate;<sup>97</sup> and butyl mercaptan adds to perfluorocyclobutene, giving 1:1 adducts and 2:1 adducts with and without loss of HF.<sup>106</sup>



### Addition of RSCl to Olefins

The free radical addition of  $\text{CF}_3\text{SCl}$  to trifluoroethylene, vinylidene fluoride, hexafluoropropylene, trifluorovinyl methyl ether, and vinyl chloride has been studied.<sup>40</sup> The reaction was initiated by ultraviolet radiation, x-rays, and with azonitrile catalyst. Both possible 1:1 adducts are formed, in each case, the predominant orientations with respect to the  $\text{CF}_3\text{S}$  group were usually opposite to that reported for the radical additions of  $\text{CF}_3\text{SH}$ .<sup>42</sup> A mechanism based upon the assumption that the chlorine atom is the major adding species has been proposed to account for these orientations.

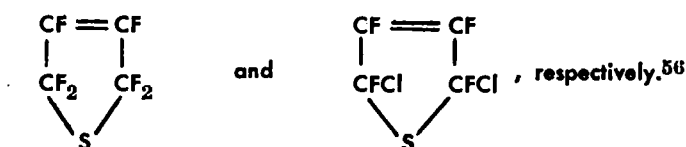


An addition, presumably ionic, of  $\text{CF}_3\text{SCl}$  to vinyl chloride is also accomplished by heating a mixture of the reactants in acetonitrile at  $100^\circ$ .<sup>40</sup> In this case, only one isomer is formed.

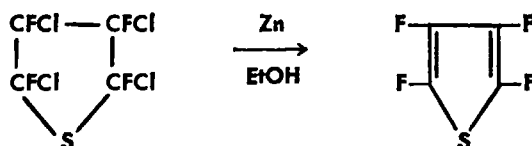


Other ionic additions of sulfonyl chlorides to olefins include the addition of  $\text{CF}_3\text{SCl}$  to ethylene;<sup>40</sup>  $\text{CF}_2\text{ClSCl}$  to 1,1-difluoroethylene and cyclohexene;<sup>61</sup>  $\text{EtSCl}$  and  $\text{CH}_3\text{CHClCH}_2\text{SCl}$  to vinylidene fluoride;<sup>61</sup> and  $\text{CF}_2\text{ClCF}_2\text{SCl}$  to cyclohexene.<sup>59</sup>

Fluorine-containing sulfides can also be prepared by the related addition of sulfur chlorides to fluoroolefins. When tetrafluoroethylene is heated with either  $\text{SCl}_2$  or  $\text{S}_2\text{Cl}_2$  at  $100\text{--}150^\circ$ ,  $(\text{CClF}_2\text{CF}_2)_2\text{S}$ , in mixture with the di- and trisulfides and  $\text{CF}_2\text{ClCF}_2\text{SCl}$  is obtained.<sup>59, 105</sup> Perfluorobutadiene and 1,4-dichlorobutadiene react with sulfur monochloride to give

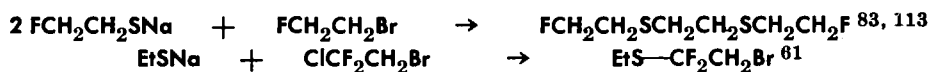
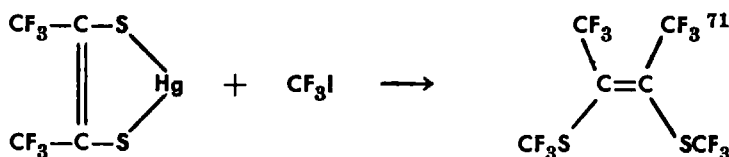


The latter cyclic sulfide is converted to perfluorothiophene by first chlorinating and then dechlorinating the tetrachloride by zinc in ethanol.



### Nucleophilic Displacement

Fluoroalkyl sulfides have been prepared by reaction of alkyl halides with sodium and mercuric mercaptides, as follows:



Sulfides are also prepared by reaction of sodium salts of thiophenols with alkyl halides:

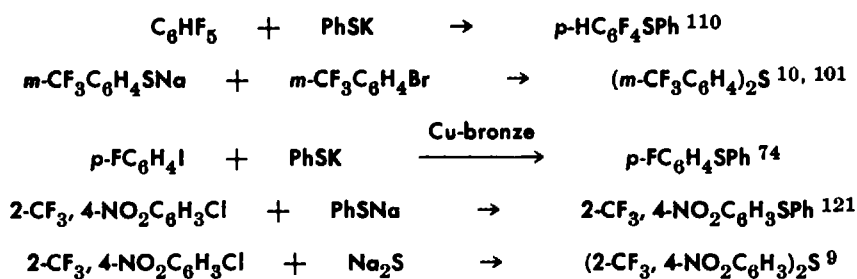


Alkyl tosylates with KSH also give sulfides.

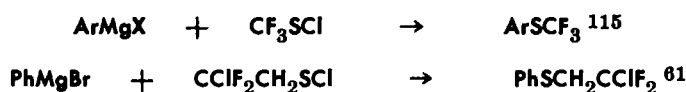


A number of alkyl aromatic sulfides and diaryl sulfides have been prepared by the reaction of aryl halides with salts of mercaptans, thiophenols, or sodium sulfide. For example:



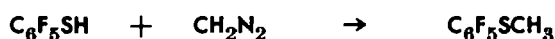


The reaction of aryl Grignard reagents with sulfenyl chlorides gives sulfides also.



### From Diazomethane

Perfluorothiophenol has been methylated with diazomethane.<sup>110</sup>

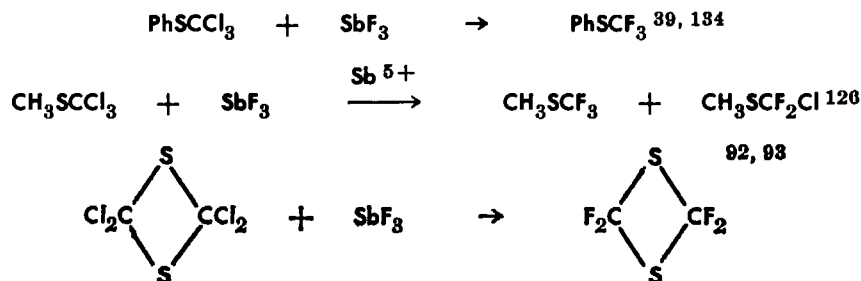


Sulfenyl chlorides also react with diazomethane to give sulfides.<sup>61</sup>

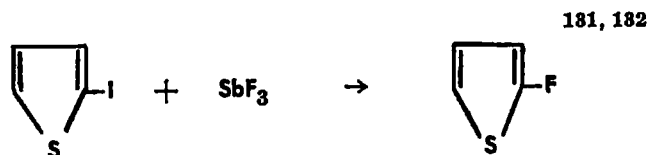


### Halogen Exchanges

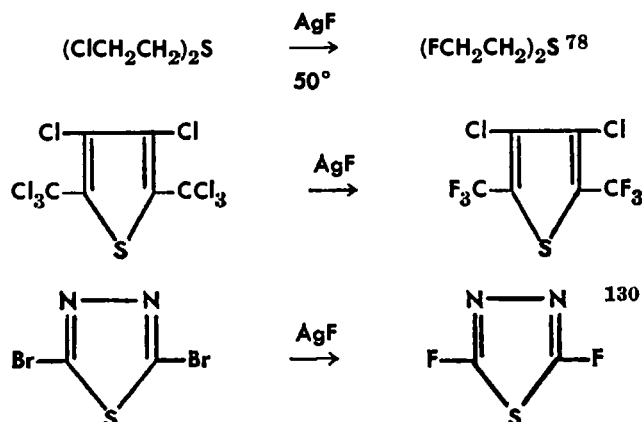
Fluorine-containing sulfides can be prepared by halogen-exchange reactions in which the corresponding chlorine- or bromine-containing sulfides are treated with metal fluorides. Antimony trifluoride has been used most often as the source of fluoride, either by itself or with a catalytic amount of a penta-valent antimony salt added (Swartz Reaction). The reaction usually proceeds without solvent, but polar solvents such as nitromethane<sup>131</sup> or tetramethylene sulfone<sup>93</sup> have been used to advantage.



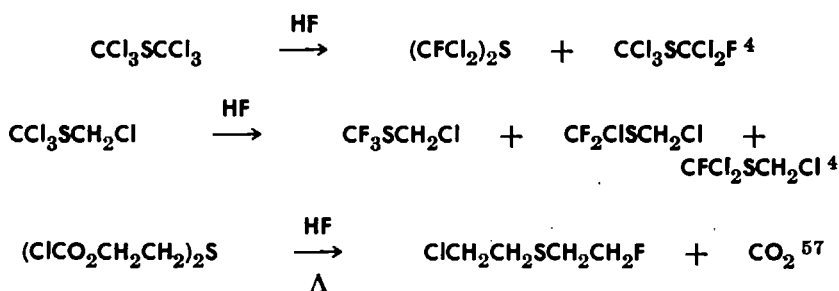




Silver fluoride has been used to effect substitution for chlorine and bromine, both in aliphatic and in heterocyclic sulfides.

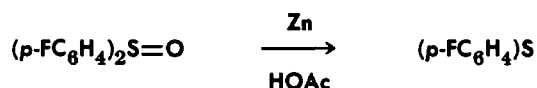


Anhydrous hydrogen fluoride has also been used to convert chlorosulfides to fluorosulfides.

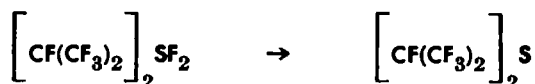


#### From Tetravalent Sulfur Compounds

*p*-Fluorophenyl sulfide is prepared by the reduction of the corresponding sulfoxide with zinc in acetic acid.<sup>74</sup>

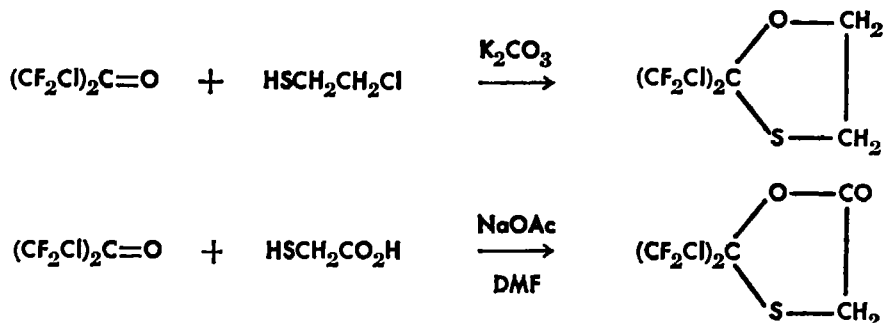


Perfluoroisopropyl sulfide is formed by an unusual reaction: treating bis(perfluoroisopropyl) sulfur difluoride with titanium tetrachloride.<sup>112</sup>

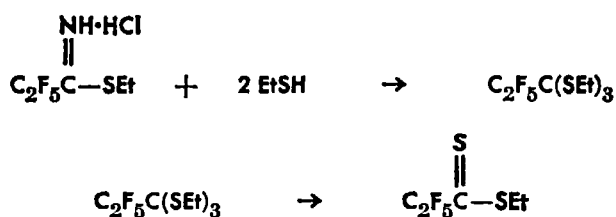


### Thioketals and Thioöorthoesters

Thioketals and thioöorthoesters can be regarded as sulfides. The monothioethyleneketal of *s*-dichlorotetrafluoroacetone is produced by the base-induced ketalization of the ketone with 2-chloroethylenethiol.<sup>119</sup> The ketone with mercaptoacetic acid gives a similar cyclic product.



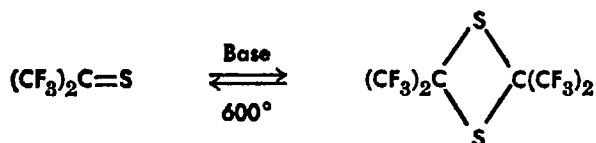
Perfluoroalkyl trithioöorthoesters are prepared by mercaptolysis of perfluoroalkylimidothioester hydrochlorides under pressure at elevated temperature.<sup>7</sup> The corresponding dithioesters that are formed as by-products in this reaction can be accounted for by a subsequent reaction of the thioöorthoesters with hydrogen chloride.



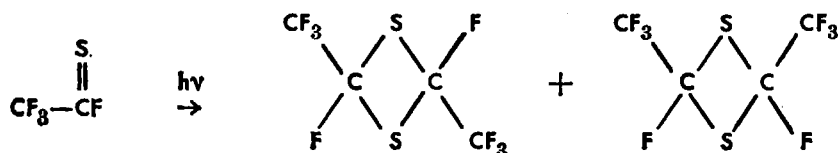
### DIMERIZATION AND POLYMERIZATION OF THIOCARBONYL COMPOUNDS

Polyfluorothioketones, such as hexafluorothioacetone and perfluorobutane-2-thione, dimerize spontaneously at 25° in a few hours to give 1,3-dithietanes.<sup>54, 93, 94, 95</sup> Bases catalyze this dimerization so that it proceeds rapidly even at -78°. Even weak bases such as dimethylformamide and diethyl ether are effective catalysts for this dimerization. The 1,3-dithietanes can be pyro-

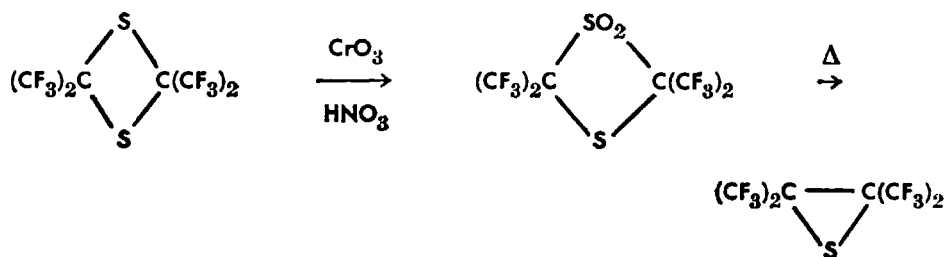
lyzed back to the monomeric thioketone at temperatures between 400–650°.



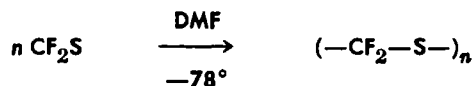
Certain other fluorine-containing thiocarbonyl compounds, including dithioesters and thioacid chlorides such as  $\text{CF}_3\text{CS}_2\text{CF}_3$  and  $\text{CF}_2\text{ClCSCl}$ , also undergo spontaneous or base-catalyzed dimerization. Many of the fluorinated thiocarbonyl compounds that do not dimerize spontaneously can be dimerized by irradiation with ultraviolet light.<sup>93, 95</sup> For example,  $\text{CF}_3\text{CSF}$  and several other thioacyl fluorides and chlorides have been dimerized to a mixture of the *cis*- and *trans*-1,3-dithietanes in this manner.



Like most perfluoroalkyl sulfides, the 1,3-dithietanes are quite resistant to oxidation. They can, however, be oxidized to the sulfide-sulfone by chromium trioxide in refluxing fuming nitric acid.<sup>11, 91</sup> Pyrolysis at 500° converts these sulfide-sulfones to episulfides by loss of sulfur dioxide.<sup>91</sup>



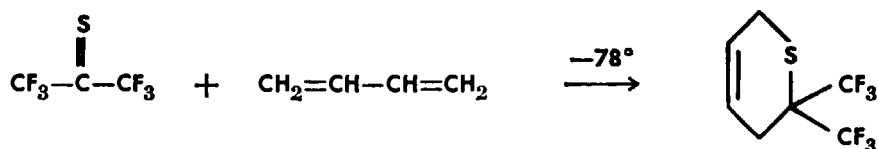
A number of thiocarbonyl compounds will polymerize. By use of anionic initiators at low temperatures (–78°C.), thiocarbonyl fluoride is converted to a tough, high molecular weight elastomer.<sup>92</sup>



Other thioacyl fluorides, such as  $\text{CF}_3\text{CSF}$ ,<sup>86</sup>  $\text{CHF}_2\text{CSF}$ ,<sup>43</sup> and  $\text{NCCSF}$ <sup>104</sup> are polymerized in a similar manner. At temperatures below  $-100^\circ$ , polymers can also be obtained from perfluorothioketones.<sup>87, 91</sup>

### DIELS ALDER REACTIONS OF THIOCARBONYL COMPOUNDS

Perfluorothiocarbonyl compounds are among the most active dienophiles ever investigated in the Diels-Alder diene reaction.<sup>88, 89, 93, 94</sup> Hexafluorothioacetone reacts instantaneously with butadiene at  $-78^\circ$  to give high yields of a dihydrothiopyran, the normal Diels-Alder adduct. This reaction is so fast it can actually be used to titrate butadiene in an inert solvent using the appearance of the blue color of the thioketone as the end point of the titration.

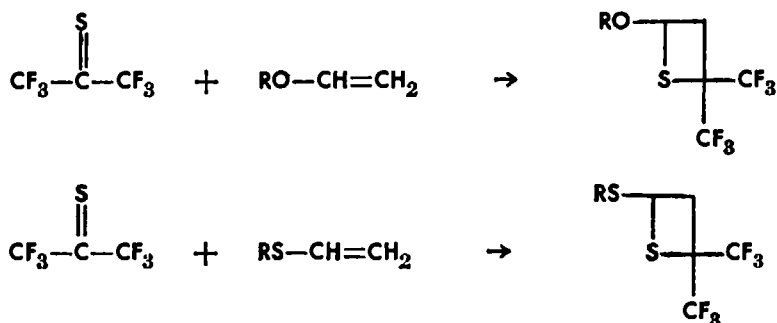


Other conjugated dienes and certain aromatic compounds containing diene units, such as furan, anthracene, and even styrene, also react to give cyclic adducts at low temperature.<sup>89, 93</sup>

A number of other fluorine-containing thiocarbonyl compounds also react rapidly with dienes or aromatic systems to give cyclic adducts.<sup>89, 93</sup> Some of these dienophiles include  $\text{S}=\text{CF}_2$ ,<sup>20, 86</sup>  $\text{CF}_3\text{CSF}$ ,  $\text{CF}_3\text{CS}_2\text{CH}_3$ ,  $\text{S}=\text{C}(\text{SCF}_3)_2$ ,<sup>88</sup> and  $\text{S}=\text{CF}(\text{CN})$ .<sup>104</sup>

### OTHER REACTIONS OF THIOCARBONYL COMPOUNDS

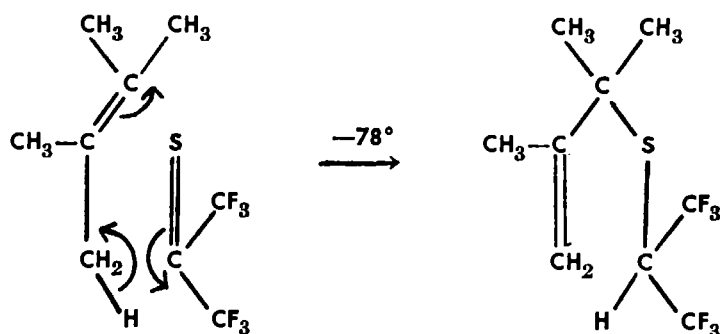
Hexafluorothioacetone adds to electron-rich olefins, such as vinyl ethers or vinyl sulfides, to form thietanes in a cyclo-addition reaction similar to the Diels-Alder reaction.<sup>90, 91</sup>



Hexafluorothioacetone combines with olefins that have allylic hydrogen atoms to give allyl sulfides.<sup>93</sup>

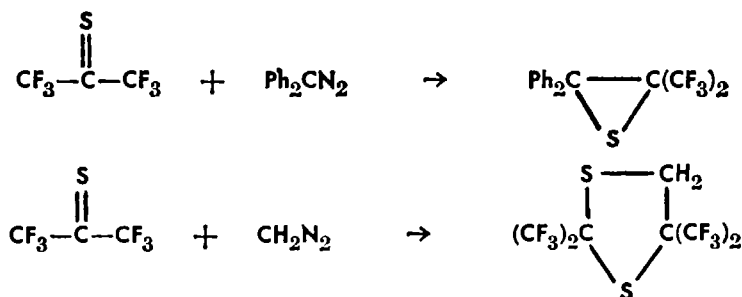


This reaction proceeds very rapidly, even at  $-78^\circ$ . A cyclic mechanism has been proposed for this reaction.<sup>90, 94</sup>

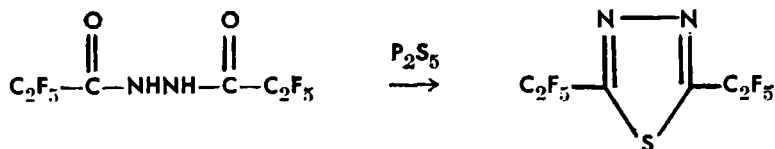


Diene polymers, such as polyisoprene (crepe rubber) are modified by a similar reaction with hexafluorothioacetone.<sup>84</sup>

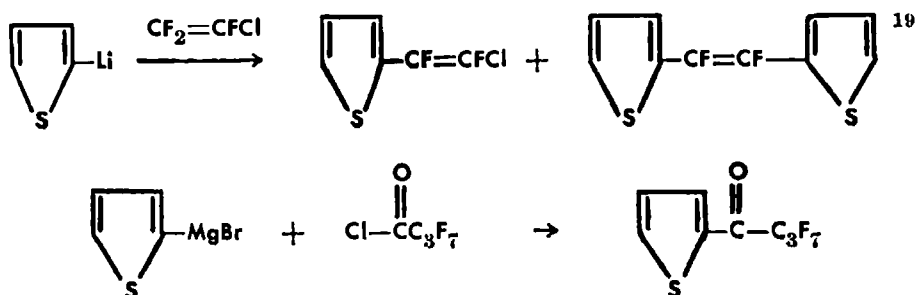
Cyclic sulfides are obtained from the reaction of diazocompounds with hexafluorothioacetone. Diphenyldiazomethane and ethyl diazoacetate give episulfides, and diazomethane gives a 1,3-dithiolane.<sup>96</sup>



Fluoroalkyl thiadiazoles are prepared by heating *bis*(fluoroacyl)hydrazines with an excess of phosphorus pentasulfide at  $200-300^\circ\text{C}$ .<sup>15, 16</sup>



Thiophenes with fluorine-containing groups can be prepared from thienyl lithium and thienyl magnesium bromide.



### Disulfides and Polysulfides

The perfluoroalkyl di-, tri-, and tetrasulfides are more stable than their unfluorinated analogs.<sup>44</sup> The disulfides are resistant to oxidising reagents. Perfluorodimethyl disulfide is not affected by fuming nitric acid.<sup>45</sup> This acid has actually been used to remove traces of the trisulfide from n-perfluoropropyl disulfide.<sup>125</sup> The perfluoroalkyl di- and polysulfides, however, are easily decomposed by basic reagents to give fluoride ions.<sup>5, 44</sup>

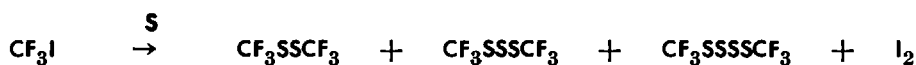
When heated to 200° or above, the perfluoroalkyl disulfides dissociate into free radicals. Radicals generated by this method have been used to initiate the polymerization of hexafluoropropylene.<sup>24</sup>

The perfluoroalkyl di- and polysulfides have much lower boiling points than their corresponding fluorine-free analogs. For example, (CF<sub>3</sub>S)<sub>2</sub> boils at 34° and (CF<sub>3</sub>S)<sub>2</sub>S at 86°, compared to 110° for (CH<sub>3</sub>S)<sub>2</sub> and 170° for (CH<sub>3</sub>S)<sub>2</sub>S.

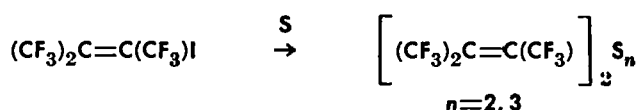
### PREPARATION

#### *Fluoroalkyl Iodides with Sulfur*

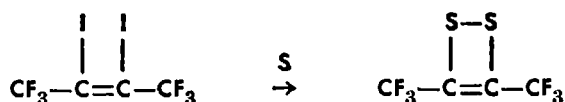
Fluoroalkyl disulfides and higher polysulfides are prepared by heating fluoroalkyl iodides with sulfur at temperatures from 200°–300°. Perfluorodimethyl disulfide and the corresponding tri- and tetrasulfides are prepared by this method.<sup>2, 5, 44</sup>



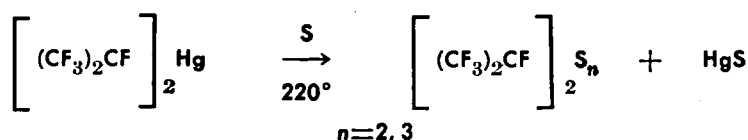
Perfluoroethyl,<sup>86</sup> perfluoro-n-propyl,<sup>47, 50, 62, 125</sup> perfluoroisopropyl,<sup>14</sup> (C<sub>2</sub>F<sub>5</sub>)(CF<sub>3</sub>)CF-,<sup>54, 95</sup> (C<sub>4</sub>F<sub>9</sub>)(CF<sub>3</sub>)CF-,<sup>49</sup> and H(CF<sub>2</sub>)<sub>6</sub>CH<sub>2</sub>-<sup>31</sup> di- and polysulfides have been prepared in a similar manner from the corresponding iodides and sulfur. An unsaturated disulfide and trisulfide have also been prepared:<sup>64</sup>



Reaction of hexafluoro-2-butyne diiodide with sulfur gives an unsaturated cyclic disulfide.<sup>64</sup>

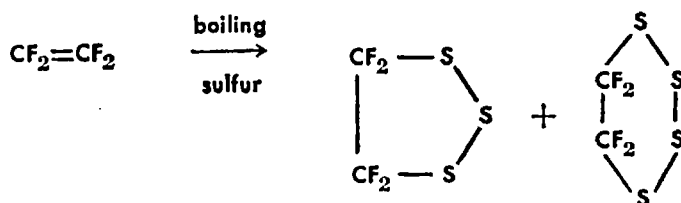


Perfluoroalkyl mercurials will also react with sulfur to give di- and trisulfides.<sup>54, 87, 95</sup>

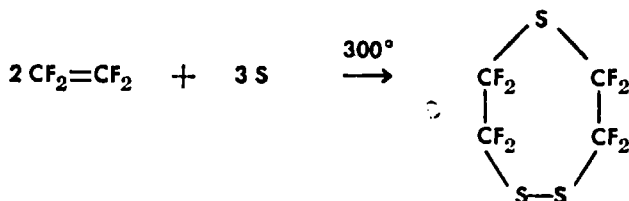


### *Fluoroolefins and Fluoroacetylenes with Sulfur*

The reaction of tetrafluoroethylene with sulfur to produce octafluoro-1,4-dithiane was discussed earlier. Conducting this reaction in a flow system at atmospheric pressure by passing tetrafluoroethylene gas through boiling sulfur (ca. 445°) gives mainly cyclic polysulfides.<sup>65, 69</sup> Tetrafluoro-1,2,3-trithiolane in 10% yield and tetrafluoro-1,2,3,4-tetrathiane in 60% yield have been prepared in this manner.

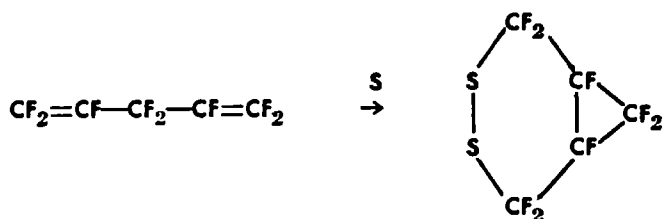


Tetrafluoroethylene and sulfur also give a trithietane when heated together at 300° in a pressure vessel for short periods of time.<sup>69</sup>

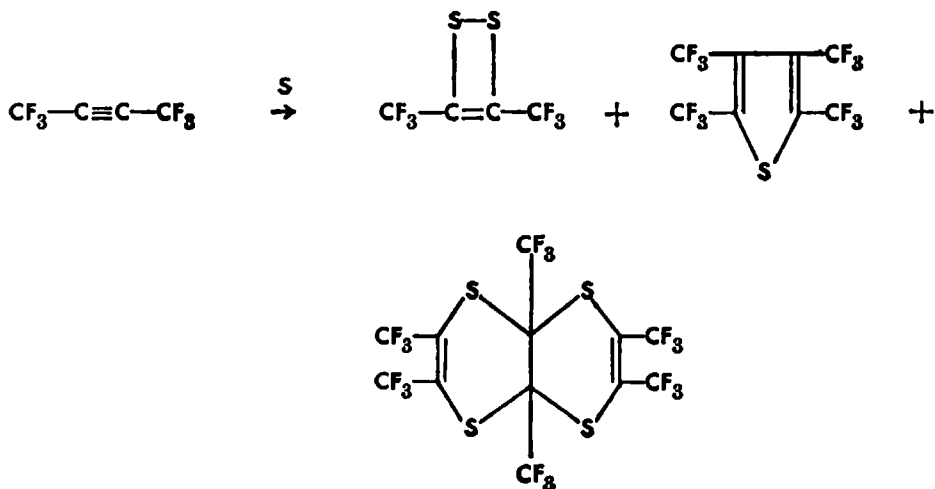


All of these cyclic polysulfides will polymerize, either spontaneously or upon initiation with basic reagents. Tough, white homopolymers of high molecular weight can be obtained from the tetrathiane, but the polymer is unstable under ambient conditions.

An unusual cyclic disulfide has been reported to be formed from the reaction of perfluoro-1,4-pentadiene and sulfur at 300°:<sup>3</sup>

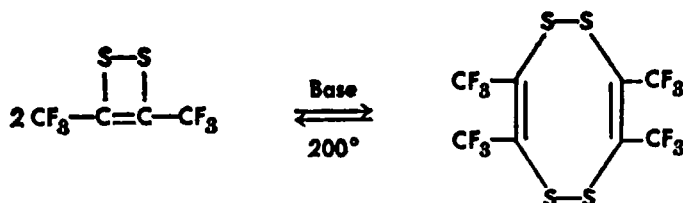


*Bis*(fluoroalkyl)acetylenes react with sulfur to give unsaturated cyclic disulfides.<sup>64, 67, 72</sup> For example, hexafluoro-2-butyne reacts with sulfur at one atmosphere and 445° in a flow system to give high yields of 3,4-*bis*-(trifluoromethyl-1,2-dithietene. Reaction of this butyne with sulfur at 200° in a sealed tube gives, in addition to the dithietene, an 11% yield of *tetrakis*(trifluoromethyl)-thiophene and a 29% yield of 2,3,4a,6,7,8a-*hexakis*(trifluoromethyl)-4a,8a-dihydro-*p*-dithiino(2,3,6)-*p*-dithiin.



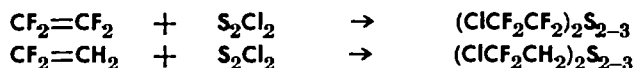


The dithietene is dimerized to a cyclic 8-membered disulfide by the presence of a basic catalyst such as triethylamine. The dimer is reconverted to the monomeric dithietene at 200°.

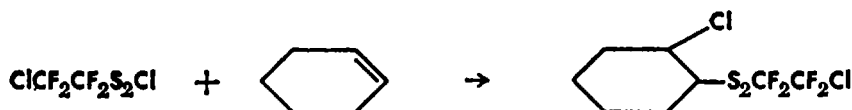


### Sulfur Monochloride with Fluoroolefins

Chlorofluoroalkyl di- and trisulfides are prepared by the addition of sulfur monochloride to tetrafluoroethylene<sup>59, 105</sup> and vinylidene fluoride<sup>61</sup> at temperatures from 100–125°.

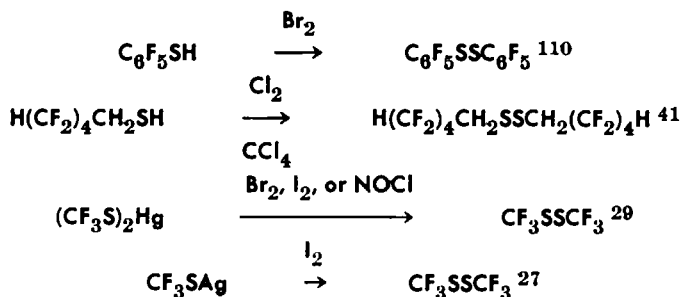


Other products, including  $\text{ClCF}_2\text{CF}_2\text{SCl}$  and  $\text{ClCF}_2\text{CF}_2\text{SSCl}$ , can also be isolated from the tetrafluoroethylene reaction. The thio-sulfonyl chloride prepared in this reaction adds to cyclohexene to give a disulfide.<sup>59</sup>



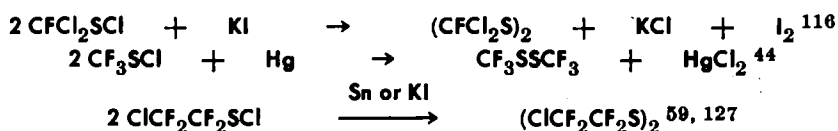
### Oxidation of Thiols

The most common method for the preparation of aliphatic and aromatic disulfides is by oxidation of the corresponding thiols. This method, however, has not been used often in the preparation of fluorine-containing disulfides, probably because the thiols are usually more difficult to prepare than the disulfides. A few such oxidations have been accomplished, however:



### Disulfides from Sulfenyl Chlorides

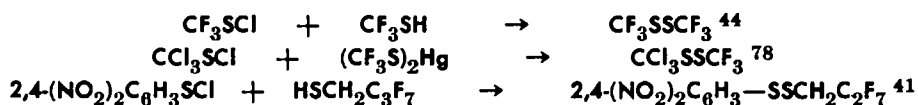
Fluorinated sulfenyl chlorides have been reduced to disulfides with potassium iodide, mercury, and tin.



The treatment of  $\text{CCl}_3\text{SCI}$  with sodium fluoride in tetramethylene sulfone also results in some disulfide in addition to the halogen-exchange product.<sup>128</sup>



Sulfenyl chlorides also react with fluoromercaptans or their salts to give disulfides.



### Aryl Halides with Sodium Disulfide

A number of fluorine-containing aromatic disulfides have been prepared from aryl halides by fusing the halide with a mixture of sodium sulfide and sulfur<sup>9, 53, 111</sup> or by heating the halide in dimethylformamide solution with sodium disulfide.<sup>101</sup>

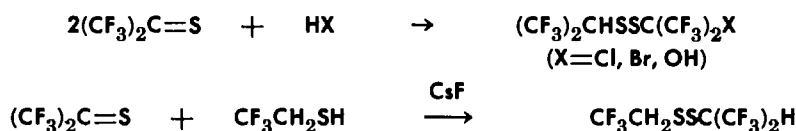


A somewhat related reaction is the preparation of  $(\text{CF}_3\text{CH}_2)_2\text{S}_2$  and  $(\text{CF}_3\text{CH}_2)_2\text{S}_3$  by heating the tosylate of the corresponding alcohol with sodium thiosulfate.<sup>1,5</sup>

### Disulfides From Thiocarbonyl Compounds

Hexafluorothioacetone can be converted to disulfides by a variety of methods.<sup>93, 94, 96</sup> Reduction of the thioketone with aqueous hydrogen iodide and ionic addition of  $\text{HCl}$ ,  $\text{HBr}$ , water and  $\text{CF}_3\text{CH}_2\text{SH}$  to the thioketone give disulfides.

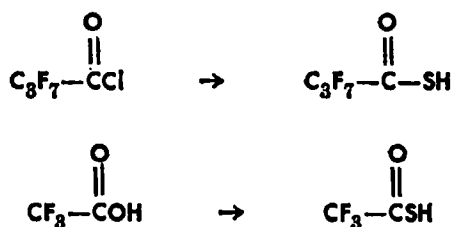




Thiophosgene, when treated with sodium fluoride in tetramethylenesulfone, was converted to  $\text{CF}_3\text{SSCF}_3$ .<sup>128</sup> This disulfide is also prepared by the reaction of carbon disulfide with iodine pentafluoride at  $195^\circ$ ,<sup>44</sup> and mercuric fluoride at  $460^\circ$ .<sup>98</sup>

### Thiol Acids

Perfluorothiol acids are prepared by the direct reaction of hydrogen sulfide on perfluoroacyl chlorides or anhydrides at  $200^\circ$ , or by reaction of  $\text{P}_2\text{S}_5$  on the perfluoro acid itself.<sup>117</sup>



Fluorothioacids have also been prepared by the hydrolysis of the  $\alpha,\alpha$ -difluoromercaptans obtained from hydrogen sulfide and fluoroolefins.<sup>33, 34</sup>

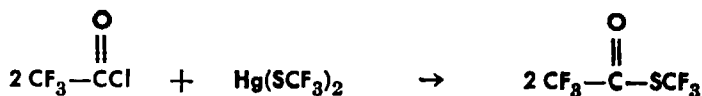


### Thiol Esters

#### PREPARATION

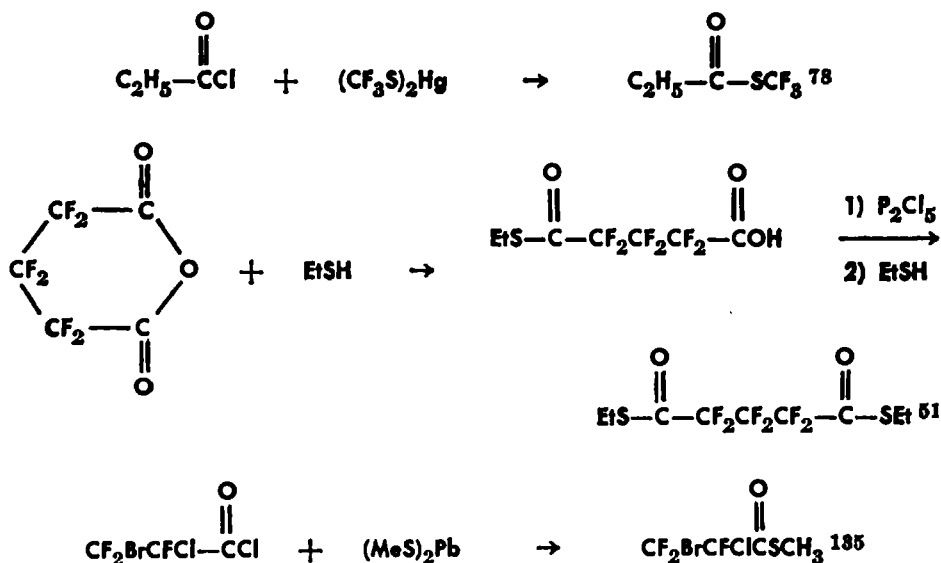
##### *From Acyl Chlorides or Anhydrides*

Trifluoroacetyl chloride reacts with  $(\text{CF}_3\text{S})_2\text{Hg}$  to give trifluoromethyl trifluorothiolacetate.<sup>78</sup>

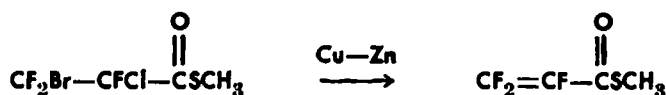


Other thiol esters with fluorine substituents in either the acyl or the alkyl portion of the ester have been prepared from the action

of acyl halids or anhydrides on thiols or their metal salts.<sup>51, 78, 113, 135</sup>

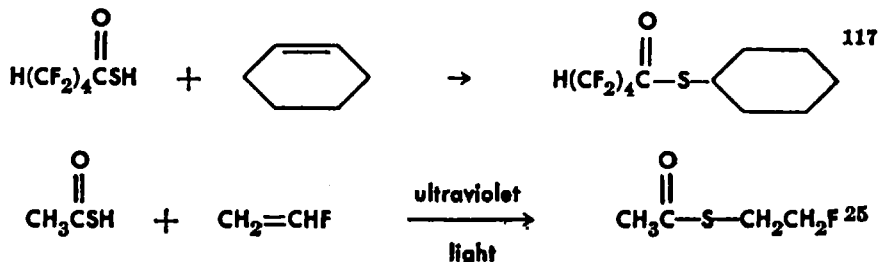


Methyl trifluorothiolacrylate has been prepared by dehalogenation of the appropriate thiol ester with zinc-copper.<sup>135</sup>



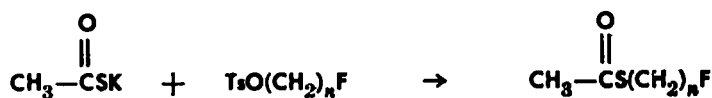
#### Addition of Thiol Acids to Olefins

Thiol acids add to olefins to give thioesters:



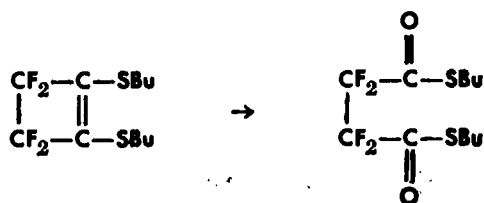
#### Nucleophilic Displacements

A series of  $\omega$ -fluoroalkyl thiolacetates have been prepared by reaction of potassium thiolacetate with  $\omega$ -alkyl tosylates<sup>55</sup> or bromides.<sup>36</sup>



### *Oxidation of Dithiolcyclobutanes*

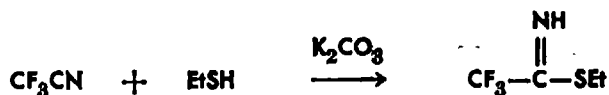
Oxidation of 1,2-bis(butylthiol)tetrafluorocyclobutane with potassium permanganate in glacial acetic acid gives the dibutyl ester of tetrafluorodithiolsuccinic acid.<sup>107</sup> This reaction illustrates the resistance to oxidation exhibited by the sulfur atom in fluoroalkyl sulfides.



### MISCELLANEOUS ESTERS

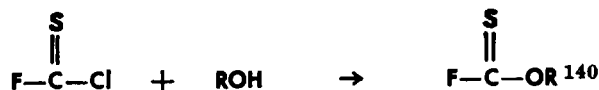
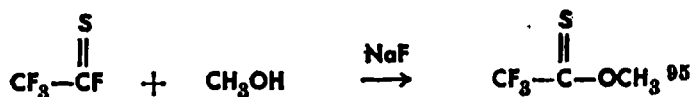
#### *Imidothiol Esters*

Imidothiol esters are formed by the potassium carbonate-catalyzed addition of thiols to perfluoroalkyl nitriles.<sup>6</sup>



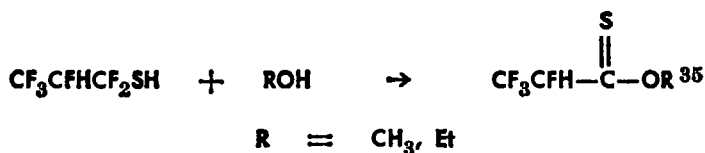
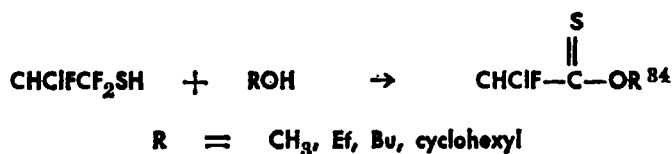
#### *Thion- and Thion-thiolesters*

Yellow thion esters are prepared by reaction of fluoroalkyl thioacyl halides with alcohols or phenols.

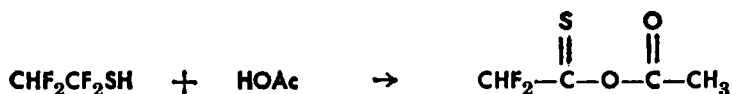


Related thione esters are prepared by reaction of alcohols with the  $\alpha,\alpha$ -difluoroalkyl thiols formed from hydrogen sulfide and

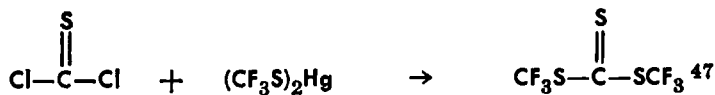
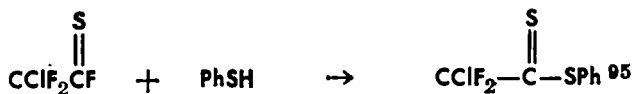
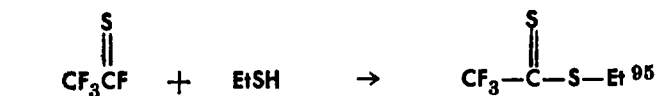
fluoroolefins. These thiols are in reality precursors to thioacyl fluorides.



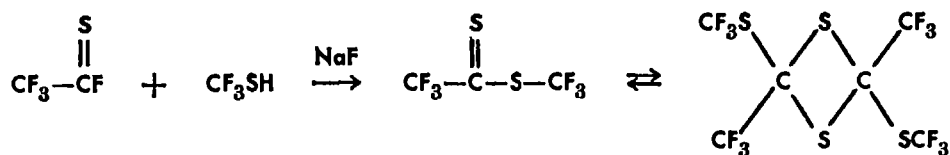
Monothione anhydrides are prepared by a similar reaction with acetic acid.<sup>34</sup>



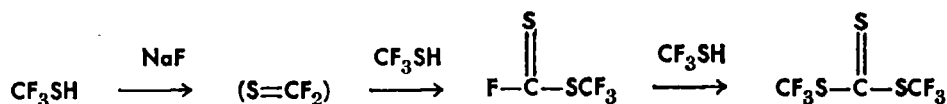
Fluorine-containing dithioesters are deep red malodorous liquids. They are prepared in reactions analogous to those used to prepare the thion esters, except that thiols are used in place of the alcohols or phenols.



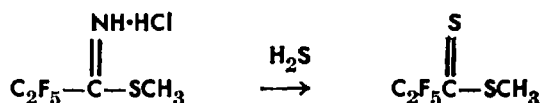
Perfluoromethyl perfluorodithioacetate, which spontaneously dimerizes, is prepared by reaction of trifluoroacetyl fluoride with trifluoromethanethiol.<sup>95</sup> The dimer of this ester can be pyrolyzed to the monomer at 600°.



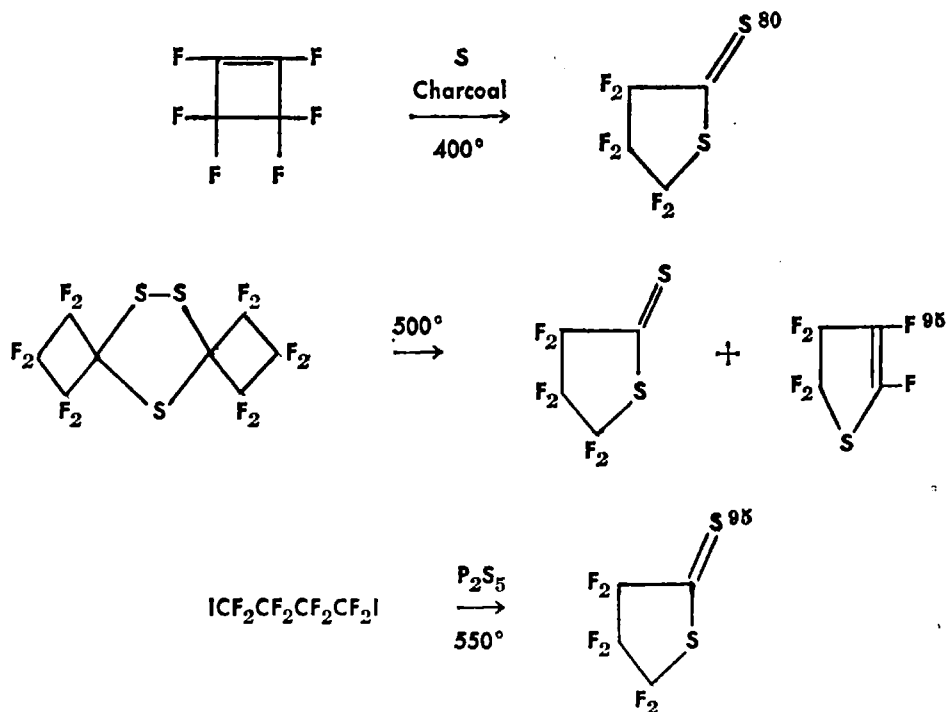
Dehydrofluorination of  $\text{CF}_3\text{SH}$  with basic reagents such as sodium fluoride<sup>77</sup> or ammonia<sup>47</sup> results in the formation of trifluoromethyl dithiofluoroformate and bis-(trifluoromethyl) trithiocarbonate. Thiocarbonyl fluoride has been postulated as an intermediate in this reaction.<sup>47</sup>



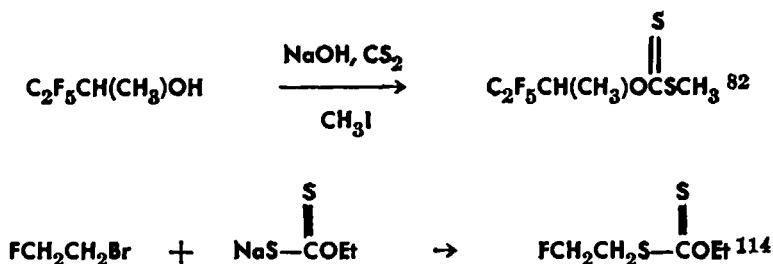
The reaction of hydrogen sulfide with the hydrochlorides of imidothioesters appears to be another general method for preparing fluorine-containing dithioesters.<sup>7</sup>



The wine-red dithiolactone, perfluorodithiobutyrolactone, has been prepared by several different methods:

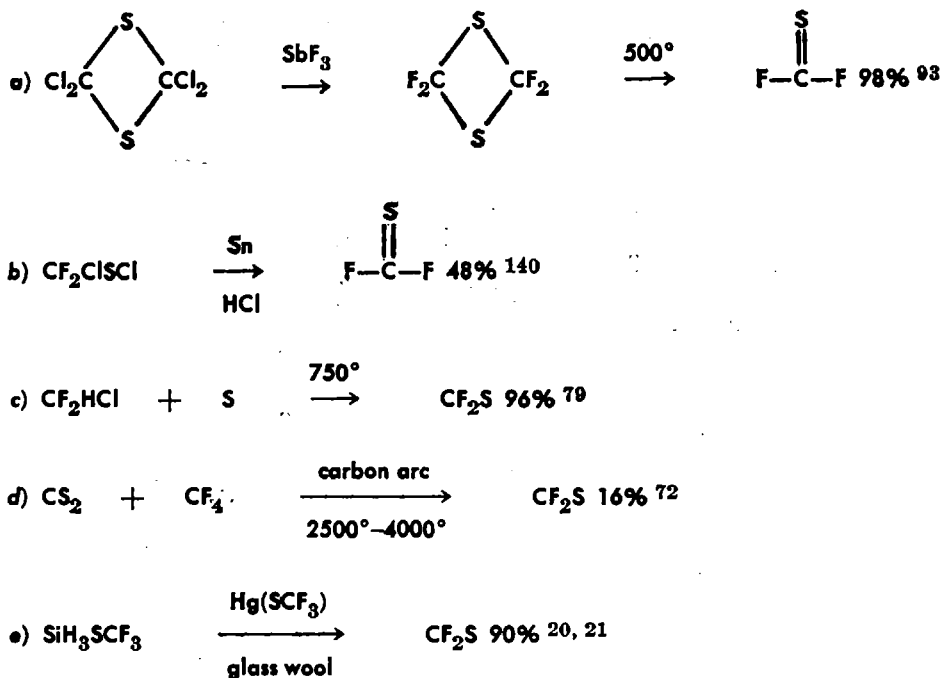


Fluoroalkyl xanthate esters have been prepared by conventional means, as follows:



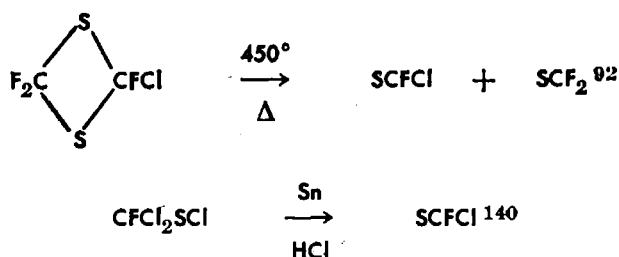
### Thioacyl Halides

Thiocarbonyl fluoride is a low-boiling colorless gas that undergoes reactions typical of acid fluorides. It was first prepared in low yield and impure form by direct reaction of carbon disulfide with elemental fluorine.<sup>129</sup> Subsequently, it has been prepared by a number of different methods. Some of these methods result in high yields of pure product.



Two of these methods have also been used to prepare thiocarbonyl chlorofluoride, bright yellow, b.p.  $10^\circ$ , that behaves chemically very much like thiocarbonyl fluoride.





Although no thioacyl halides have been reported for alkylthiocarboxylic acids, a number of thioacyl halides are known for the corresponding fluoroalkylthiocarboxylic acids. These fluorothioacyl fluorides are yellow gases or low-boiling liquids. Trifluorothioacetyl fluoride, the first member of a series of perfluoroalkylthiocarboxylic acid fluorides, is a bright yellow gas, condensing to a liquid at  $-21^\circ$ . It has been prepared by a variety of methods, several of which are applicable to the preparation of other thioacyl fluorides. Dehydrofluorination of perfluoroethanethiol with sodium fluoride at room temperature affords high yields of  $\text{CF}_3\text{CSF}$ .<sup>95</sup>



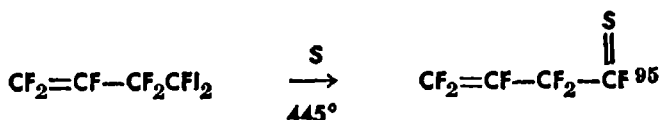
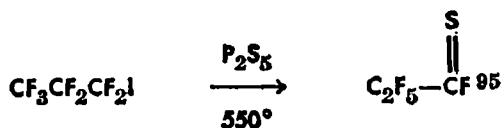
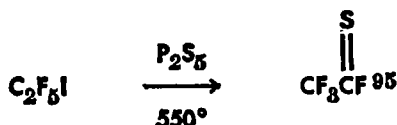
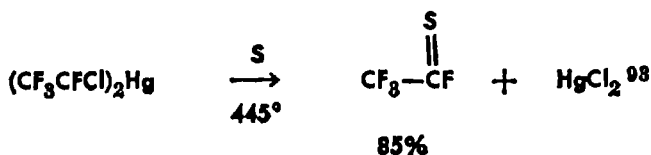
Similar dehydrofluorination of other  $\alpha,\alpha$ -difluoroalkylthiols have given the following products:  $\text{C}_2\text{F}_5\text{CSF}$ ,<sup>95</sup>  $\text{CHClFCSF}$ ,<sup>43</sup>  $\text{CF}_2\text{HCSF}$ ,<sup>43</sup>  $\text{CH}_3\text{OCHFCSF}$ ,<sup>43</sup> and  $\text{CF}_2\text{ClCSF}$ .<sup>95</sup>

Trifluorothioacetyl fluoride is also prepared by the catalytic sulfurization of tetrafluoroethylene at  $350\text{--}450^\circ$  over activated charcoal.<sup>80</sup>

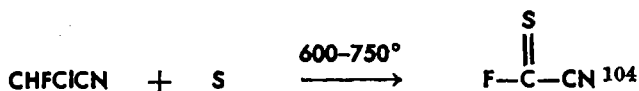


Fluoroethylenes containing other halogens react even more readily with sulfur vapors. Chlorotrifluoroethylene<sup>80, 92</sup> and bromotrifluoroethylene<sup>92</sup> react with boiling sulfur at atmospheric pressure without catalyst to give high yields of  $\text{CF}_2\text{ClCSF}$  and  $\text{CF}_2\text{BrCSF}$ , respectively.

Reaction of perfluoroalkyl derivatives of mercury or iodine with boiling sulfur or phosphorus pentasulfide appears to be another general method for the preparation of thioacyl fluorides.



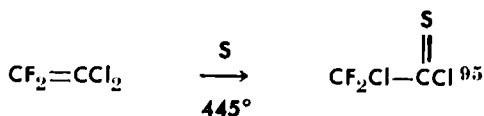
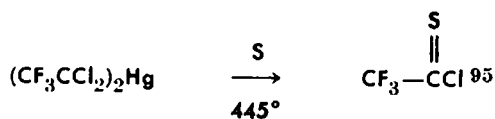
Thiocarbonyl fluorocyanide is prepared by a related reaction of  $\text{CHClFCN}$  with sulfur vapors in a hot tube.



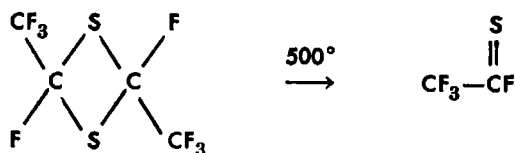
Chlorodifluorothioacetyl fluoride is prepared by reduction of  $\text{CF}_2\text{ClCF}_2\text{SCl}$  with tin and hydrochloric acid,<sup>136</sup> a reaction similar to the preparation of thiophosgene from tin and  $\text{CCl}_3\text{SCl}$ .

Fluorothioacyl chlorides are more intensely colored than are the corresponding fluorothioacyl fluorides. Most of the chlorides are bright red, whereas the fluorides are yellow.  $\text{CF}_2\text{ClCSCl}$  has maximum absorption at 510 mμ; the corresponding acid fluoride absorbs at 425 mμ.<sup>95</sup>

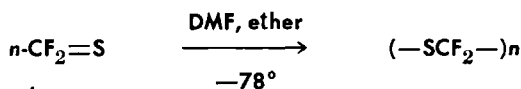
The thioacyl chlorides are prepared similarly to the fluorides.



Both the fluorothioacyl chlorides and fluorides can be prepared by pyrolysis of their cyclic dimer, but this method is usually of no practical value because the dimers are prepared from the monomeric halides, themselves.<sup>95</sup>

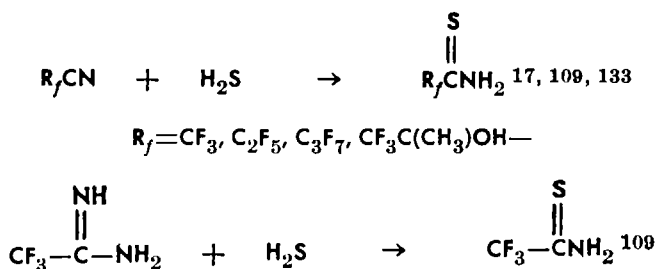


Many of the fluorine-containing thioacyl halides can be polymerized by basic reagents at low temperatures to homopolymers of high molecular weight containing thioacetal linkages.<sup>43, 86, 92, 104</sup> For example, thiocarbonyl fluoride is polymerized in ether to a tough, resilient elastomer by initiation with dimethyl formamide at  $-78^\circ$ .<sup>86</sup> Other monomers, such as  $\text{FCSCN}$ ,<sup>104</sup>  $\text{CF}_2\text{HCSF}$ ,<sup>43</sup> and  $\text{CF}_3\text{CSF}$ <sup>92</sup> have been polymerized by similar methods.

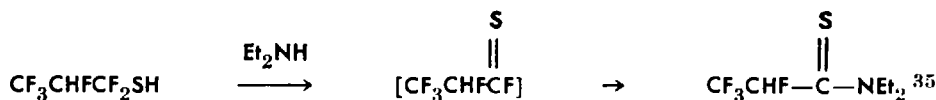


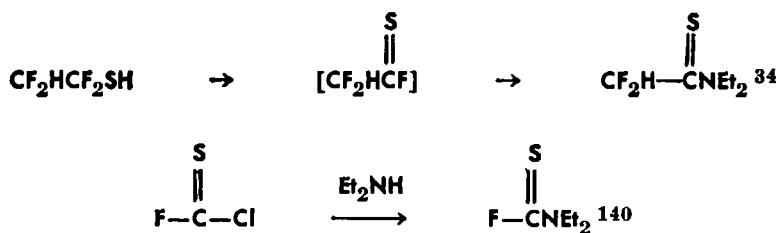
### Thioamides

Perfluorothioamides are prepared by the addition of hydrogen sulfide to perfluoronitriles, and by reaction of hydrogen sulfide with perfluoroamidines.



The reaction of thioacyl halides or  $\alpha,\alpha$ -difluorothiols (precursors to thioacyl fluorides) with secondary amines gives N-disubstitued thioamides.

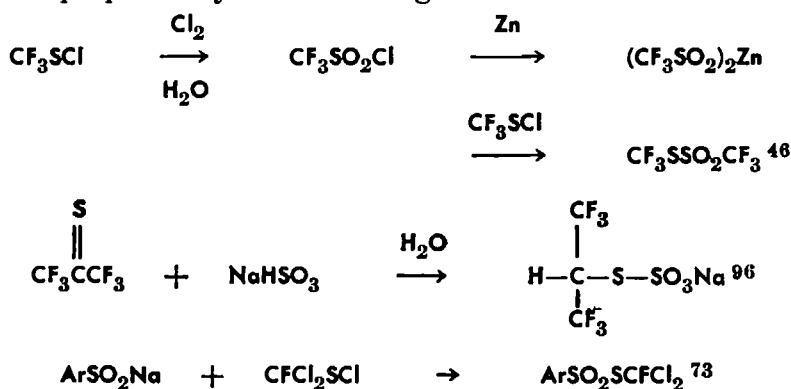




The reaction of carbonyl fluoride with  $(\text{Me}_2\text{NCS})_2\text{S}_2$  gives the thioamide,  $\text{Me}_2\text{NCSF}$ .<sup>32</sup>

### Thiosulfate Esters

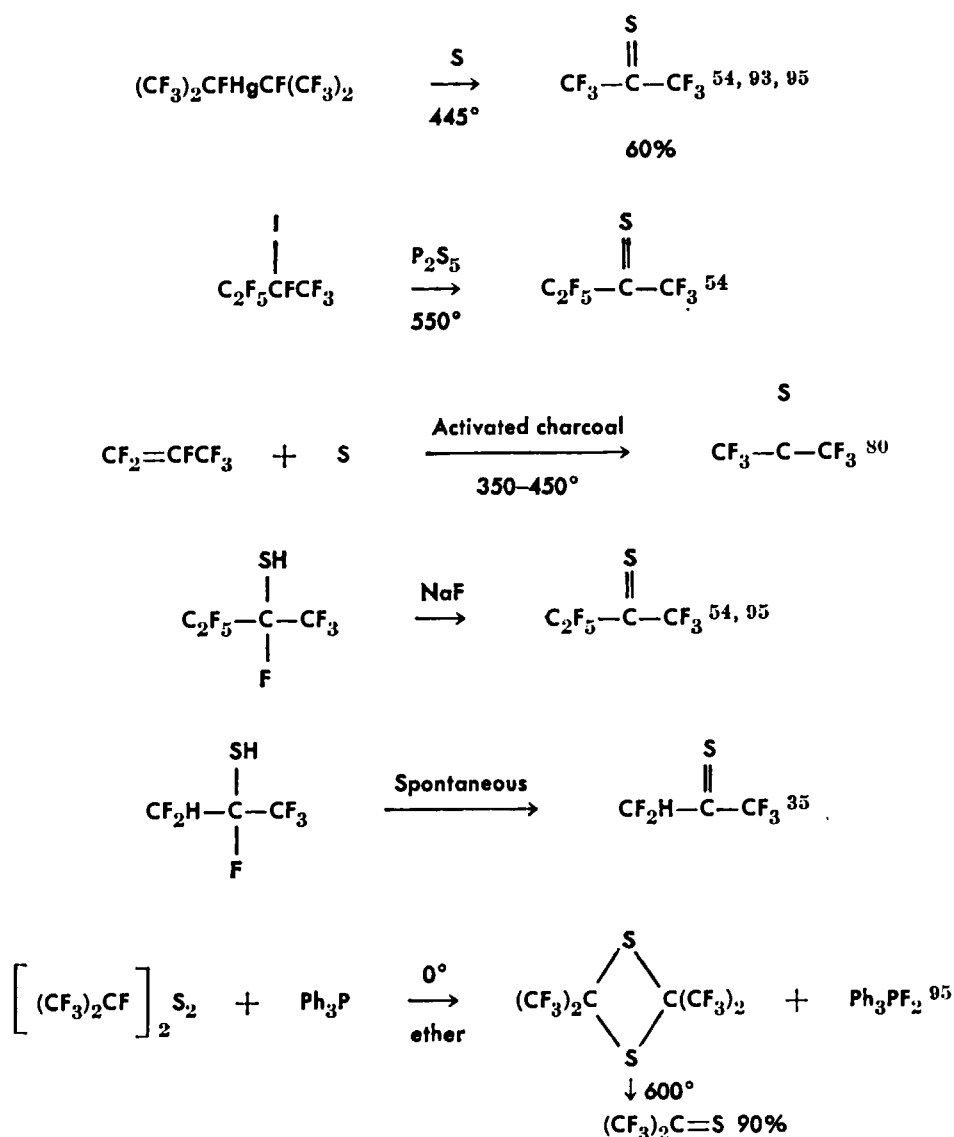
Fluoroalkyl esters of thiosulfuric acid and benzenethiosulfonic acids are prepared by the following reactions:



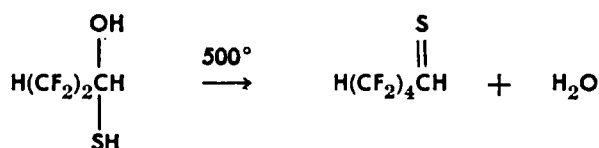
### Thioketones and Thioaldehydes

Perhaps the most unusual of all the bivalent sulfur-fluorine compounds are the perfluorothioketones. Hexafluorothioketone is an exceptionally reactive deep blue liquid, b.p.  $8^\circ$ ,  $\lambda_{\text{max}}$  580 m $\mu$ . It is not sensitive to water or to oxygen but dimerizes in the presence of base. Hexafluorothioketone is one of the most active dienophiles ever examined,<sup>88, 89</sup> and it reacts at low temperatures with olefins containing allylic hydrogen atoms to give allyl sulfides.<sup>84, 85, 90</sup> In many reactions of the thioketone, the  $\text{C}=\text{S}$  group behaves as though the sulfur is more electrophilic than the carbon. For example, hexafluorothioketone reacts with aqueous bisulfite ion to give a Bunte salt,<sup>93</sup> and with thiols to give disulfides.<sup>91, 96</sup> These and other reactions of thioketones are described in other sections of this chapter.

The following methods have been used to prepare fluoroalkyl thioketones.



Polyfluorothioaldehydes have been prepared by thermally cracking fluoroaldehyde-hydrogen sulfide adducts at  $500^\circ$  and 1–2 mm pressure.<sup>38,5</sup> These thioaldehydes are deep purple, unstable liquids that polymerize rapidly.

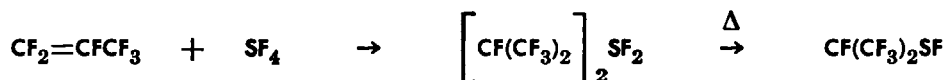


### Sulfenyl Halides

Fluorine-containing alkyl sulfenyl halides are considerably more stable than their fluorine-free analogs. This class of compounds is represented by fluoroalkyl sulfenyl fluorides, chlorides, and bromides. The sulfenyl halides that possess no  $\alpha$ -hydrogens are particularly stable and can be stored indefinitely without decomposition. Even the  $\beta$ -perfluoroalkyl sulfenyl halides appear to be quite stable.<sup>41</sup> The general behavior of the fluoroalkyl sulfenyl halides resembles that of the known alkyl and aryl sulfenyl halides.<sup>28</sup>

#### SULFENYL FLUORIDES

Sulfenyl fluorides are unknown except in the perfluoroalkyl series. The pyrolysis of  $(\text{CF}_3)_2\text{CFSF}_2\text{CF}(\text{CF}_3)_2$  at  $200^\circ$  gives the sulfenyl fluoride  $(\text{CF}_3)_2\text{CFSF}$ .<sup>112</sup> The dialkylsulfur difluoride compound is prepared from addition of  $\text{SF}_4$  to hexafluoropropylene. This sulfenyl fluoride is a pale green liquid that is highly reactive toward mercury. It does not attack glass that has been thoroughly dried.

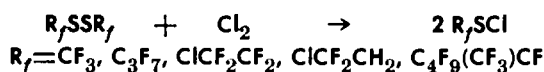


A patent has reported a product cited as  $\text{C}_8\text{F}_{17}\text{SF}$ ,<sup>118</sup> but no data supporting the composition or structure of the compound are given. The reaction of mercuric fluoride on  $\text{CCl}_3\text{SCl}$  and  $\text{C}_3\text{F}_7\text{SCl}$  is also reported to give sulfenyl fluorides,<sup>62</sup> but these results are in doubt.<sup>116</sup> A number of other workers have attempted to prepare sulfenyl fluorides without success.<sup>11, 12, 25</sup>

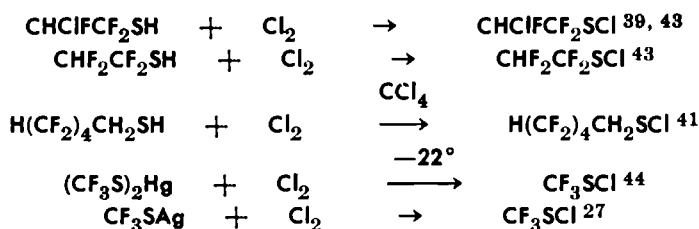
#### PREPARATION OF OTHER HALIDES

##### *Chlorination of Disulfides and Mercaptans*

A number of fluoroalkyl sulfenyl chlorides have been prepared by the chlorination of fluoroalkyl disulfides, initiated by heat or ultraviolet light.<sup>44, 49, 59, 61, 62</sup>



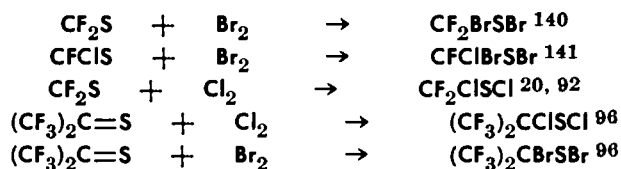
Fluoromercaptans and their salts also react with chlorine to give sulfenyl chlorides.



A fluoroalkyl sulfide,  $\text{CF}_3\text{SCH}_2\text{Cl}$ , has been chlorinated in the presence of ultraviolet light to give  $\text{CF}_3\text{SCI}$ .<sup>4</sup>

### Halogens with Thiocarbonyl Compounds

Halogens have been added across the thiocarbonyl group of fluorothiocarbonyl compounds to prepare both  $\alpha$ -chlorosulfenyl chlorides and  $\alpha$ -bromosulfenyl bromides.

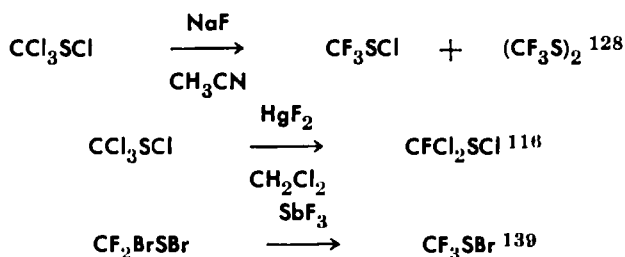


### Sulfur Chloride with Tetrafluoroethylene

The sulfenyl chloride,  $\text{CF}_2\text{ClCF}_2\text{SCI}$ , and the thiosulfenyl chloride,  $\text{CF}_2\text{ClCF}_2\text{SSCl}$ , in mixture with sulfides and polysulfides, are prepared by reacting tetrafluoroethylene with  $\text{S}_2\text{Cl}_2$  or  $\text{SCl}_2$  at  $100\text{--}120^\circ$ .<sup>59</sup>

### Halogen Exchange

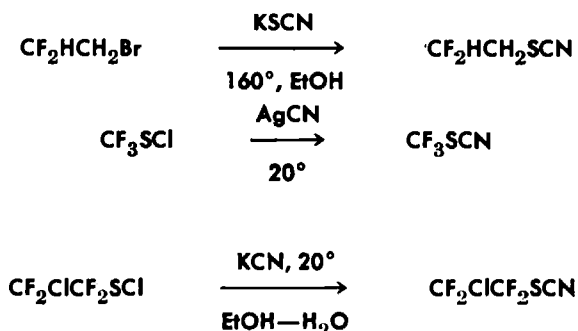
Fluoroalkyl sulfenyl chlorides and bromides are prepared by halogen-exchange reactions of chloroalkylsulfenyl halides with metal fluorides.<sup>128</sup>



Reaction of  $\text{CCl}_3\text{SNEt}_2$  with antimony trifluoride gives a 25% yield of  $\text{CF}_2\text{ClSCl}$  and a 12% yield of  $\text{CFCl}_2\text{SCl}$ .<sup>138</sup>

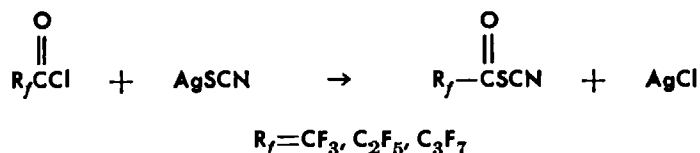
### Thiocyanates and Isothiocyanates

Fluoroalkyl thiocyanates are prepared from the corresponding fluoroalkyl bromides or tosylates by reaction with potassium thiocyanate<sup>55, 114, 137</sup> or from fluoroalkyl sulfenyl chlorides by reaction with potassium cyanide<sup>137</sup> or silver cyanide.<sup>25, 5</sup>



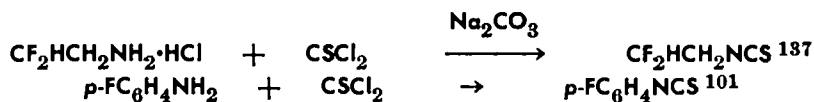
Trifluoromethylsulfenyl chloride reacts at room temperature with silver thiocyanate to give the unstable sulfenyl thiocyanate,  $\text{CF}_3\text{SSCN}$ , and with silver selenocyanate to give the selenocyanate,  $\text{CF}_3\text{SSeCN}$ .<sup>25, 5</sup>

Perfluorothioacyl thiocyanates are prepared by action of silver thiocyanate on perfluoroacyl chlorides.<sup>102</sup>



Fluoroaromatic thiocyanates have been prepared by the Sandmeyer reaction from the corresponding fluoroaromatic amines.<sup>101</sup>

The isomeric isothiocyanates are prepared by the reaction of thiophosgene with fluoroamines.



### Sulfur Attached to Other Elements

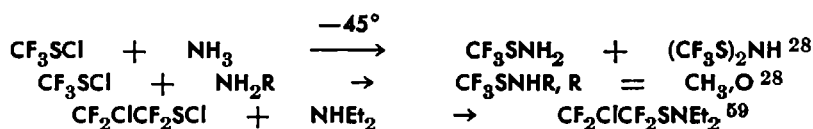
Several fluoroalkyl sulfur derivatives have been prepared, in which at least one bond of the divalent sulfur is attached to



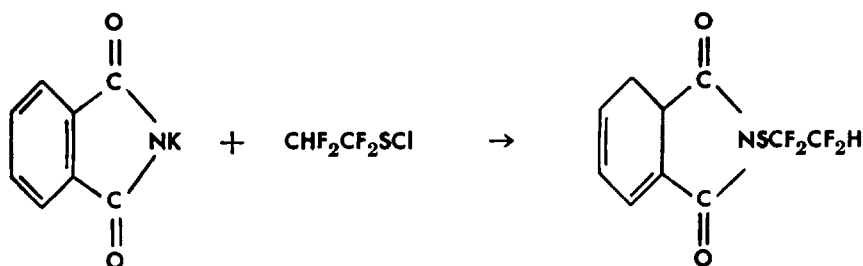
another element, such as nitrogen, phosphorus, arsenic, oxygen, or silicon.

### NITROGEN

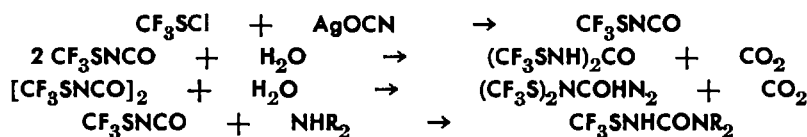
Sulfenamides are prepared by reacting fluoroalkyl sulfonyl chlorides with ammonia or with primary and secondary amines.<sup>25, 59, 61</sup>



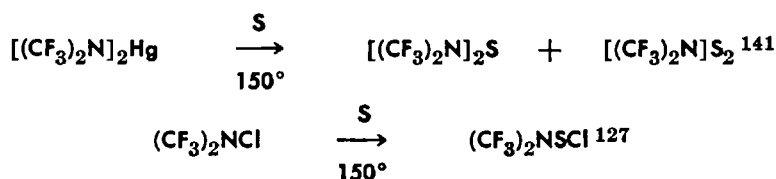
Cyclic imides also undergo a similar reaction with sulfonyl chlorides to give derivatives that have been patented as insect repellents.<sup>39</sup>

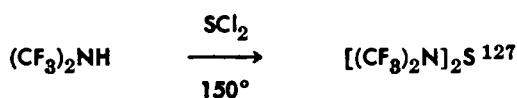


Trifluoromethanesulfonyl chloride reacts with silver cyanate to give a mixture of monomeric and dimeric trifluoromethylsulfonyl isocyanate. The isocyanate forms a trimer when heated to 100°. Reaction of water, ammonia, or amines with the isocyanate or its dimer results in the formation of ureas substituted with trifluoromethylsulfonyl groups.<sup>25a</sup>



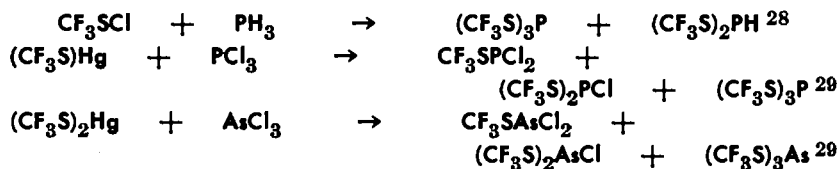
Other sulfur-nitrogen compounds have been prepared by reaction of  $[(\text{CF}_3)_2\text{N}]_2\text{Hg}$  and  $(\text{CF}_3)_2\text{NCl}$  with elemental sulfur, and by reaction of  $(\text{CF}_3)_2\text{NH}$  with sulfur dichloride.





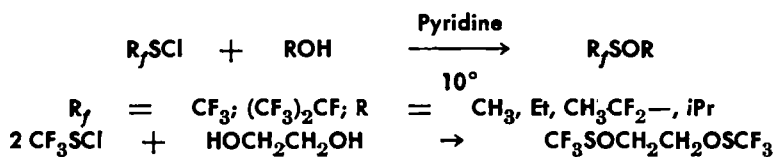
## PHOSPHORUS AND ARSENIC

Phosphorus and arsenic derivatives corresponding to the nitrogen derivatives are prepared by similar methods.



## OXYGEN

Fluoroalkyl thioperoxides are prepared by base catalyzed reactions of fluoroalkyl sulphenyl chlorides with alcohols.<sup>1</sup>



A *bis* (perfluoroalkyl) thioperoxide has been prepared by an unusual reaction of a *bis* (perfluoroalkyl) sulfur difluoride with boric oxide.<sup>112</sup>



## SILICON

Silyl iodide reacts with  $\text{Hg}(\text{SCF}_3)_2$  to give  $\text{SiH}_3\text{SCF}_3$ . This compound is unstable and can be decomposed over glass wool to give thiocarbonyl fluoride.<sup>20, 21</sup>



## Physical Properties of Bivalent Sulfur-Fluorine Compounds

## THIOLS

C<sub>1</sub>

$\text{CF}_3\text{SH}$ , b.  $-36.7$ ; <sup>43</sup> Mercuric salt, b<sub>3</sub>  $55^\circ$ , b<sub>125</sub>  $120^\circ$ ; <sup>78</sup> m.  $328^\circ$ , <sup>98</sup>  $37.5$ , <sup>5</sup>  $39-40^\circ$ ; <sup>78</sup> d 25/0 (solid) 2.911, d 45.4/0 2.98.<sup>78</sup>

C<sub>1</sub>

CClF<sub>2</sub>CF<sub>2</sub>SH, b. 33°. <sup>86, 95</sup>

CF<sub>3</sub>CF<sub>2</sub>SH, b. -6° to -4°. <sup>86, 95</sup>

CHBrFCF<sub>2</sub>SH, b<sub>150</sub> 42-6°. <sup>43</sup>

CHClFCF<sub>2</sub>SH, b. 66-7°, <sup>43</sup> 64°; <sup>34</sup> n 25/D 1.3791, <sup>43</sup> n 0/D 1.3880; <sup>34</sup> d 0/4 1.4750. <sup>34</sup>

CHF<sub>2</sub>CF<sub>2</sub>SH, b. 25-7°, <sup>43</sup> 31°; <sup>34</sup> n 0/D 1.3230; <sup>34</sup> d 0/4 1.4910. <sup>34</sup>

CClF<sub>2</sub>CH<sub>2</sub>SH, b. 75-6°; n 20/D 1.405; d 20/20 1.344. <sup>61</sup>

CF<sub>3</sub>CH<sub>2</sub>SH, b. 34-5°, 36.5°; <sup>41</sup> n 26/D 1.3426, <sup>1.5</sup> n 25/D 1.3413. <sup>41</sup>

CHF<sub>2</sub>CHF<sub>2</sub>SH, b<sub>100</sub> 20-2°. <sup>43</sup>

CF<sub>3</sub>CH(OH)SH, b<sub>80</sub> 51°; n 25/D 1.3879. <sup>38</sup>

CHF<sub>2</sub>CH<sub>2</sub>SH, b. 64°, <sup>43</sup> 62-3°; <sup>35</sup> n 24/D 1.3920, <sup>43</sup> n 20/D 1.3930; <sup>35</sup> d 20/4 1.2465. <sup>35</sup>

CH<sub>3</sub>CF<sub>2</sub>SH in mixture with CHF<sub>2</sub>CH<sub>2</sub>SH, b. 60-2°; d 20/4 1.2362; n 20/D 1.4040. <sup>35</sup>

CH<sub>2</sub>FCH<sub>2</sub>SH, b<sub>206</sub> 35-6°, <sup>43</sup> b<sub>225</sub> 38.5°; <sup>25</sup> n 25/D 1.4284, <sup>43</sup> 1.4288; <sup>25</sup> d 25/4 1.082. <sup>25</sup>

C<sub>3</sub>

CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>SH, b<sub>759</sub> 23.7°, <sup>47</sup> b. 25-6°. <sup>95</sup>

(CClF<sub>2</sub>)<sub>2</sub>CHSH, b. 115°; n 25/D 1.4018. <sup>41</sup>

CF<sub>3</sub>CFHCF<sub>2</sub>SH, b. 42-3°; n 20/D 1.3279; d 20/4 1.4766. <sup>35</sup>

(CF<sub>3</sub>)<sub>2</sub>CHSH, b. 44°. <sup>96</sup>

CF<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>SH, b. 45-7°; n 25/D 1.3285. <sup>41</sup>

CF<sub>3</sub>CF<sub>2</sub>CH(OH)SH, b<sub>66</sub> 56°; n 25/D 1.3611. <sup>38</sup>

CH<sub>3</sub>OCHFCH<sub>2</sub>SH, b<sub>17</sub> 14-6°; n 25/D 1.3733. <sup>43</sup>

F(CH<sub>2</sub>)<sub>3</sub>SH, b<sub>749</sub> 100-1°; n 25/D 1.4355. <sup>55</sup>

C<sub>4</sub>

CF<sub>3</sub>CF<sub>2</sub>CF(CF<sub>3</sub>)SH, b. 53°. <sup>95</sup>

CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>SH, b. 75-6°; n 25/D 1.3217. <sup>41</sup>

CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CH(OH)SH, b<sub>46</sub> 54°; n 25/D 1.3507. <sup>38</sup>

CH<sub>3</sub>SC(CF<sub>3</sub>)<sub>2</sub>SH, b<sub>85</sub> 56-7°; n 25/D 1.3936. <sup>96</sup>

CHF<sub>2</sub>CF<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)SH, b. 86-8°. <sup>37</sup>

C<sub>5</sub>

(CF<sub>3</sub>CF<sub>2</sub>)<sub>2</sub>CHSH, b. 86.5-87°; n 25/D 1.3101. <sup>41</sup>

(CF<sub>3</sub>CF<sub>2</sub>)<sub>2</sub>C(OH)SH, b<sub>56</sub> 41°; n 25/D 1.3251. <sup>38</sup>

H(CF<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>SH, b. 127°, b<sub>0.5</sub> 84°; n 25/D 1.3688. <sup>41</sup>

H(CF<sub>2</sub>)<sub>4</sub>CH(OH)SH, b<sub>17</sub> 69-71°; n 25/D 1.3669. <sup>38</sup>

HSCH<sub>2</sub>(CF<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>SH, b<sub>25</sub> 92-93.5°; n 25/D 1.4215. <sup>41</sup>

$\text{CH}_2\text{ClSCCl}_2\text{F}$ , b.  $149^\circ$ ,  $b_{12}$   $43^\circ$ ; n 20/D 1.4960.<sup>4</sup>

$\text{CH}_3\text{SCClF}_2$ ,  $b_{755}$   $56.3^\circ$ ; m.  $-100.2^\circ$ ; n 20/D 1.3926; d 20/4 1.298.<sup>4</sup>

$\text{CH}_3\text{SCF}_3$ ,  $b_{750}$   $11.5-11.7^\circ$ .<sup>128</sup>

$\text{CH}_2\text{ClSCHF}_2$ , b.  $99^\circ$ ; n 20/D 1.4356.<sup>4</sup>

### C<sub>3</sub>

$\text{CF}_3\text{SCClFCClF}_2$ , b.  $84^\circ$ ; n 24/D 1.3560.<sup>40</sup>

$\text{CF}_3\text{SCClFCClF}_2$ , in mixture with  $\text{CF}_3\text{SCF}_2\text{CCl}_2\text{F}$ , b.  $76-82^\circ$ ; n 25/D 1.3561.<sup>40</sup>

$\text{CF}_3\text{SCHFCClF}_2$ , b.  $54^\circ$ ; n 25/D 1.3237.<sup>40</sup>

$\text{CF}_3\text{SCF}_2\text{CHClF}$ , b.  $67^\circ$ ; <sup>40,42</sup> n 25/D 1.3334,<sup>40</sup> 1.3339–1.3341.<sup>42</sup>

$\text{CF}_3\text{SCF}_2\text{CHF}_2$ , b.  $33^\circ$ .<sup>42</sup>

$\text{CF}_3\text{SCF}_2\text{CH}_2\text{Cl}$ , b.p.  $79^\circ$ ; n 26.5/D 1.3521.<sup>40</sup>

$\text{CF}_3\text{SCH}_2\text{CClF}_2$ , b.p.  $71^\circ$ ; n 26.5/D 1.3456.<sup>40</sup>

$\text{CF}_3\text{SCClFCClF}_2$ , b.  $84^\circ$ ; n 25/D 1.3560.<sup>40</sup>

$\text{CF}_3\text{SCHFCHF}_2$ , b.  $52^\circ$ ; n 25/D 1.3112–1.3119.<sup>42</sup>

$\text{CF}_3\text{SCHClCH}_2\text{Cl}$ , b.  $122^\circ$ ; n 24/D 1.4213.<sup>40</sup>

$\text{CF}_3\text{SCH}_2\text{CHCl}_2$ , b.  $115-6^\circ$ ; n 24/D 1.4162.<sup>40</sup>

$\text{CH}_3\text{S}-\text{CF}=\text{CClF}$ , b.  $88-9^\circ$ ; n 20/D 1.4390; d 20/4 1.4390.<sup>58</sup>

$\text{CF}_3\text{S}-\text{CH}=\text{CH}_2$ , b.  $22^\circ$ .<sup>42</sup>

$\text{CF}_3\text{SCH}_2\text{CHF}_2$ , b.  $58^\circ$ ; n 25/D 1.3270.<sup>42</sup>

$\text{CH}_3\text{SCClFCHClF}$ ,  $b_{15}$   $58.5^\circ$ ; n 20/D 1.5900; d 20/4 1.355.<sup>58</sup>

$\text{CH}_2\text{ClSCH}_2\text{CClF}_2$ ,  $b_{25}$   $57-9^\circ$ ; n 20/D 1.555; d 20/20 1.468.<sup>61</sup>

$\text{CClF}_2\text{SCH}_2\text{CH}_2\text{Cl}$ ,  $b_{76}$   $74^\circ$ ; n 19/D 1.4474; d 19/4 1.4491.<sup>139</sup>

$\text{CF}_3\text{SCH}_2\text{CH}_2\text{Cl}$ , b.p.  $98^\circ$ ,<sup>139</sup>  $96^\circ$ ,<sup>40</sup>  $94-8^\circ$ ; <sup>42</sup> n 25/D 1.3939,<sup>40, 42</sup> n 16/D 1.3960;<sup>139</sup> d 19/4 1.4040.<sup>139</sup>

$\text{CH}_3\text{SCF}_2\text{CHClF}$ ,  $b_{98}$   $51^\circ$ ,<sup>42</sup> b.  $104^\circ$ ; <sup>58</sup> n 25/D 1.4024,<sup>42</sup> n 20/D 1.4083; d 20/4 1.389.<sup>58</sup>

$\text{CH}_3\text{SCF}_2\text{CHF}_2$ , b.  $63^\circ$ ; n 8/D 1.3675; d 8/4 1.322.<sup>58</sup>

$\text{CH}_3\text{SCHFCHF}_2$ , n 23/D 1.3889.<sup>42</sup>

$\text{CH}_3\text{SCF}_2\text{CH}_2\text{F}$ ,  $b_{85}$   $39-42^\circ$  (impure); n 23/D 1.3779.<sup>42</sup>

### C<sub>4</sub>

$(\text{CClF}_2\text{CF}_2)_2\text{S}$ , b.  $68-72^\circ$ ,<sup>105</sup>  $100-2^\circ$ ; <sup>59</sup> n 10/D 1.368; d 10/4 1.662.<sup>59</sup>

$\text{CF}_3\text{SCF}_2\text{CClFCF}_3$ , in mixture with  $\text{CF}_3\text{SCF}(\text{CF}_3)\text{CClF}_2$ , b.  $68-72^\circ$ ; n 25/D 1.3143.<sup>40</sup>

$\text{CF}_3\text{SCF}_2\text{CHFCF}_3$ , b.  $53-4^\circ$ .<sup>42</sup>

$(\text{CHClFCF}_2)_2\text{S}$ ,  $b_{60}$   $71.5^\circ$ ,<sup>34</sup>  $b_{62}$   $74^\circ$ ; <sup>43</sup> n 0/D 1.3920,<sup>34</sup> n 25/D 1.3897; <sup>43</sup> d 0/4 1.6350.<sup>34</sup>

- $(\text{CHF}_2\text{CF}_2)_2\text{S}$ , b.  $100-2^\circ$ ; n 20/D 1.3280; d 0/4 1.6240.<sup>34</sup>  
 $\text{CHF}_2\text{CHFSCF}_2\text{CHClF}$ ,  $b_{34}$   $51-3^\circ$ ; n 25/D 1.3750–1.3759.<sup>43</sup>  
 $\text{C}_2\text{F}_5\text{S}-\text{CH}=\text{CH}_2$ , b.  $45^\circ$ ; n 25/D 1.3510.<sup>42</sup>  
 $\text{CHF}_2\text{CHFSCF}_2\text{CHF}_2$ , b.  $104-5^\circ$ ; n 25/D 1.3383.<sup>43</sup>  
 $\text{CF}_3\text{SCF}(\text{OCH}_3)\text{CClF}_2$ , b.  $105^\circ$ ; n 25/D 1.3540.<sup>40</sup>  
 $\text{CF}_3\text{SCF}_2\text{CClFOCH}_3$ , b.  $113^\circ$ ; n 24/D 1.3528.<sup>40</sup>  
 $(\text{CClF}_2\text{CH}_2)_2\text{S}$ ,  $b_{50}$   $78^\circ$ ; n 20/D 1.4200; d 20/20 1.526.<sup>61</sup>  
 $\text{CH}_2\text{ClCH}_2\text{SCF}_2\text{CClF}_2$ ,  $b_{100}$   $85^\circ$ ; n 20/D 1.4218; d 20/4 1.538.<sup>59</sup>  
 $\text{HOOCCH}_2\text{SCF}_2\text{CHClF}$ ,  $b_{0.01}$   $85^\circ$ , n 25/D 1.4470; d 25/4 1.5847.<sup>106</sup>  
 $\text{HOOCCH}_2\text{SCF}_2\text{CHF}_2$ ,  $b_4$   $93-4^\circ$ ; n 25/D 1.4083.<sup>30</sup>  
 $(\text{CF}_3\text{CH}_2)_2\text{S}$ , b.  $82-6^\circ$ ; n 27/D 1.3370; d 1.25.<sup>1.5</sup>  
 $\text{CH}_3\text{SCF}_2\text{CHFCH}_3$ , b.  $85-7^\circ$ ; n 20/D 1.3443; d 20/4 1.380.<sup>60</sup>  
 $\text{CH}_3\text{SCF}_2\text{CFHCF}_3$  (91%) and  $\text{CH}_3\text{SC}(\text{CF}_3)\text{FCHF}_2$  (9%), b.  $84.5-86^\circ$ , n 25/D 1.3400–1.3393.<sup>42</sup>  
 $\text{CF}_3\text{SCF}_2\text{CHFOCH}_3$ , b.  $102^\circ$ ; n 25/D 1.3303–1.3307.<sup>42</sup>  
 $\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3$ ,  $b_{108}$   $59^\circ$ ; n 25/D 1.3740.<sup>42</sup>  
 $\text{C}_2\text{H}_5\text{SCF}=\text{CClF}$ , b.  $106-7^\circ$ ; n 20/D 1.4385; d 20/4 1.282.<sup>58</sup>  
 $\text{HOCH}_2\text{CH}_2\text{SCF}_2\text{CHClF}$ ,  $b_{0.5}$   $62.5^\circ$ ; n 25/D 1.4426; d 75/4 1.4793.<sup>106</sup>  
 $\text{C}_2\text{H}_5\text{SCClFCHClF}$ , b.  $138^\circ$ ; n 20/D 1.4612; d 20/4 1.425.<sup>58</sup>  
 $\text{C}_2\text{H}_5\text{SCF}_2\text{CHClF}$ ,  $b_{736}$   $120^\circ$ ,<sup>58</sup>  $b_{100}$   $69.1^\circ$ ;<sup>100</sup> n 17/D 1.4158,<sup>58</sup> n 25/D 1.4079;<sup>100</sup> d 17/4 1.331,<sup>58</sup> d 25/4 1.3212.<sup>100</sup>  
 $\text{CH}_2=\text{CHCH}_2\text{SCF}_3$ , b.  $61^\circ$ .<sup>78</sup>  
 $(\text{CHF}_2\text{CH}_2)_2\text{S}$ ,  $b_{20}$   $51-4^\circ$ ; n 24/D 1.3938–1.3944.<sup>43</sup>  
 $\text{C}_2\text{H}_5\text{SCF}_2\text{CHF}_2$ , b.  $88^\circ$ ,<sup>58</sup>  $86-88^\circ$ ;<sup>37</sup> n 18/D 1.3735; d 18/4 1.246.<sup>58</sup>  
 $\text{C}_2\text{H}_5\text{SCF}_2\text{CH}_2\text{Br}$ ,  $b_{32}$   $67-8^\circ$ ; n 20/D 1.469; d 20/20 1.505.<sup>61</sup>  
 $\text{C}_2\text{H}_5\text{SCH}_2\text{CClF}_2$ ,  $b_{30}$   $35^\circ$ ; n 20/D 1.4276; d 20/20 1.216.<sup>61</sup>  
 $\text{CH}_2\text{ClCH}_2\text{SCH}_2\text{CH}_2\text{F}$ ,  $b_{30}$   $91.5-92.5^\circ$ ; m.  $-44^\circ$ ; n 25/D 1.4852; d 20/20 1.228.<sup>57</sup>  
 $(\text{CH}_2\text{FCH}_2)_2\text{S}$ ,  $b_{30}$   $95-6^\circ$ .<sup>76</sup>
- $\text{C}_5$   
 $\text{CF}_3\text{SCF}_2\text{CF}(\text{CF}_3)\text{SCF}_3$ , b.  $100^\circ$ ; n 25/D 1.3250.<sup>40</sup>  
 $\text{CF}_3\text{S}(\text{CF}_2\text{CClF})_2\text{H}$ , b.  $145-6^\circ$ ; n 25/D 1.3627.<sup>43</sup>  
 $\text{CF}_3\text{S}(\text{CF}_2)_4\text{H}$ , b.  $84^\circ$ .<sup>43</sup>  
 $\text{CF}_3\text{S}(\text{CHFCH}_2)_2\text{H}$ , b.  $52^\circ$ ; n 25/D 1.3112–1.3119.<sup>43</sup>  
 $\text{CF}_3\text{CH}_2\text{SC}(\text{CF}_3)\text{FCHF}_2$ , b.  $98^\circ$ ; n 24/D 1.3220.<sup>43</sup>  
 $\text{CF}_3\text{CH}_2\text{SCF}_2\text{CHFCH}_3$ , b.  $105^\circ$ ; n 24/D 1.3208.<sup>43</sup>  
 $\text{CH}_3\text{OCF}(\text{SCF}_3)\text{CF}_2\text{SCF}_3$ , b.  $127^\circ$ ; n 25/D 1.3531.<sup>40</sup>

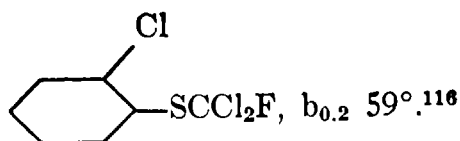
$\text{CH}_3\text{S}(\text{CF}_2\text{CClF})_2\text{H}$ ,  $b_7$   $57^\circ$ ;  $n$  25/D 1.4061.<sup>43</sup>  
 $\text{C}_2\text{F}_5\text{SCH}_2\text{CH}_2\text{SCF}_3$ ,  $b_{65}$   $55-6^\circ$ ;  $n$  24/D 1.3620.<sup>42</sup>  
 $\text{CHClFCF}_2\text{SCF}_2\text{CHFOCH}_3$ ,  $b_{0.8}$   $57-60^\circ$ ;  $n$  25/D 1.3827.<sup>43</sup>  
 $\text{C}_2\text{H}_5\text{SCF}_2\text{CHF}_2$ ,  $b_{752}$   $100-2^\circ$ ;  $n$  20/D 1.3548;  $d$  20/4 1.322.<sup>60</sup>  
 $\text{HOCH}_2\text{CH}_2\text{SCF}_2\text{CHF}_2$ ,  $b_5$   $53-4^\circ$ ;  $n$  20/D 1.3835;  $d$  20/4 1.546.<sup>60</sup>  
 $i\text{-PrSCClFCHClF}$ ,  $b_{738}$   $159^\circ$ ;  $n$  20/D 1.4534;  $d$  25/4 1.302.<sup>58</sup>  
 $\text{CH}_3\text{CHClCH}_2\text{SCH}_2\text{CClF}_2$ ,  $b_5$   $93^\circ$ ;  $n$  20/D 1.4825;  $d$  20/20 1.3903.<sup>61</sup>  
 $i\text{-PrSCF}_2\text{CHClF}$ ,  $b.$   $135^\circ$ ;  $n$  20/D 1.4178;  $d$  20/4 1.275.<sup>58</sup>  
 $i\text{-PrSCF}_2\text{CHF}_2$ ,  $b.$   $96^\circ$ ;  $n$  20/D 1.3910;  $d$  23/4 1.266.<sup>58</sup>  
 $t\text{-BuSCF}_3$ ,  $b.$   $78^\circ$ ;  $n$  25/D 1.3658.<sup>78</sup>

$\text{C}_6$


$(\text{CF}_3)(\text{CF}_3\text{S})\text{C}=\text{C}(\text{CF}_3)(\text{SCF}_3)$ ,  $b_{20}$   $73^\circ$ .<sup>71</sup>  
 $(\text{CF}_3\text{CF}_2\text{CF}_2)_2\text{S}$ ,  $b_{760}$   $87-90^\circ$ ,<sup>62</sup>  $b.$   $88^\circ$ ; <sup>125</sup>  $n$  30/D 1.2890,<sup>62</sup>  $n$  25/D 1.2872.<sup>125</sup>  
 $[(\text{CF}_3)_2\text{CF}]_2\text{S}$ ,  $b.$   $85-86^\circ$ ,<sup>112</sup>  $b_{762}$   $116.9^\circ$ .<sup>14</sup>  
 $\text{CH}_2=\text{CHCH}_2\text{SC}(\text{CF}_3)_2\text{H}$ ,  $b_{100}$   $57-8^\circ$ ;  $n$  25/D 1.3637.<sup>85, 90</sup>  
 $(\text{CH}_3\text{OCHF}_2)_2\text{S}$ ,  $b_{1.5}$   $65-5^\circ$ ;  $n$  25/D 1.3778.<sup>43</sup>  
 $\text{C}_2\text{F}_5\text{C}(\text{SCH}_3)_3$ ,  $b_{0.7}$   $86^\circ$ ;  $n$  25/D 1.4630;  $d$  25/4 1.360.<sup>7</sup>  
 $n\text{-BuSCF}_2\text{CHCl}_2$ ,  $b.$   $43^\circ$ ;  $n$  25/D 1.4545;  $d$  25/4 1.2707.<sup>106</sup>  
 $n\text{-BuSCF}_2\text{CHClF}$ ,  $b_{25}$   $71.6^\circ$ ;  $n$  25/D 1.4196;  $d$  25/4 1.2224.<sup>106</sup>

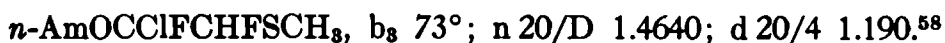
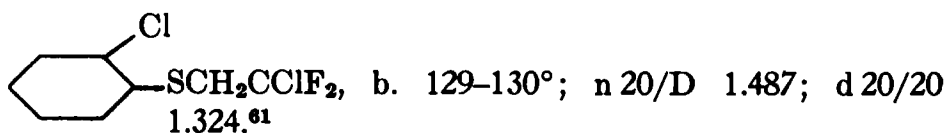
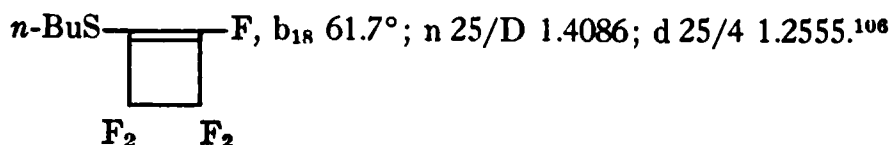
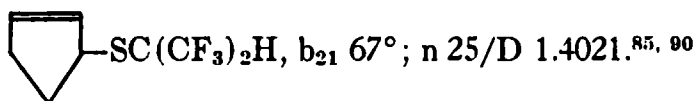
$\text{C}_7$

$\text{CF}_3\text{S}(\text{CF}_2\text{CClF})_3\text{H}$ ,  $b_{11}$   $87-90^\circ$ ;  $n$  25/D 1.3791.<sup>42</sup>  
 $\text{CF}_3\text{S}(\text{CF}_2)_6\text{H}$ ,  $b.$   $127-9^\circ$ ,  $n$  25/D 1.3008.<sup>42</sup>  
 $\text{NCCH}=\text{CHCH}_2\text{SC}(\text{CF}_3)_2\text{H}$ ,  $b.$   $75-6^\circ$ ;  $n$  25/D 1.4117.<sup>90</sup>  
 $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{SC}(\text{CF}_3)_2\text{H}$ ,  $b_{74}$   $60^\circ$ ;  $n$  25/D 1.3729.<sup>90</sup>  
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{C}(\text{SCH}_3)_3$ ,  $b_{0.7}$   $111^\circ$ ;  $n$  25/D 1.4528;  $d$  25/4 1.483.<sup>7</sup>

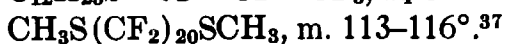
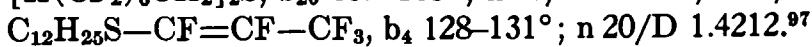
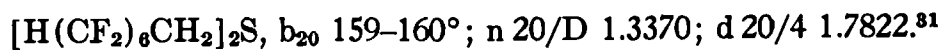
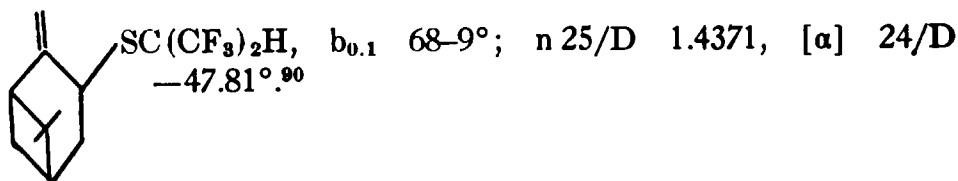
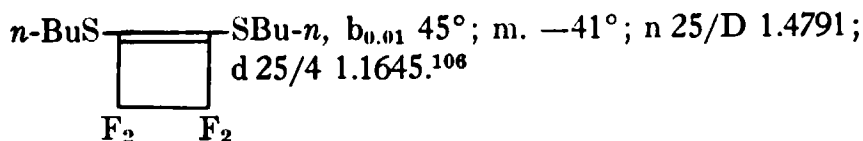
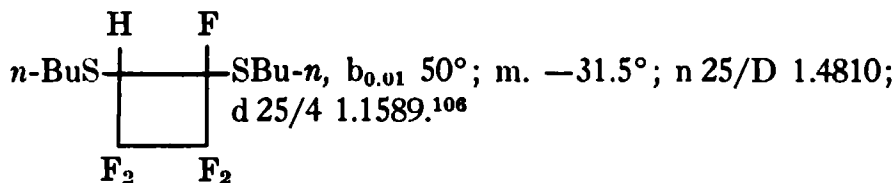
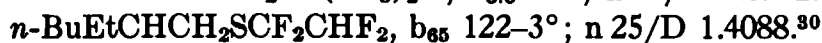
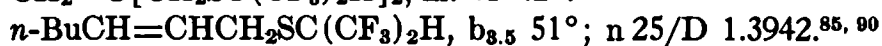
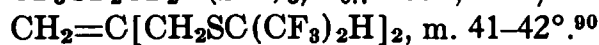
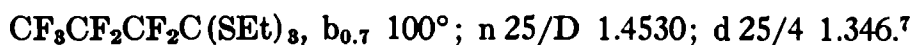
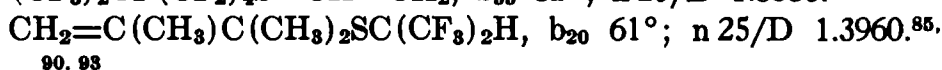


$\text{C}_8$

$\text{CF}_3\text{S}[\text{C}(\text{CF}_3)\text{FCF}_2]_2\text{SCF}_3$ ,  $b.$   $156-9^\circ$ ;  $n$  24/D 1.3314.<sup>42</sup>  
 $\text{HOOCCH}_2\text{S}$    $\text{SCH}_2\text{COOH}$ ,  $m.$   $116-117^\circ$ .<sup>106</sup>  
 $\text{PhCH}_2\text{SCF}_3$ ,  $b.$   $172^\circ$ .<sup>78</sup>



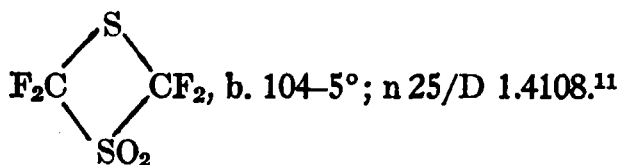
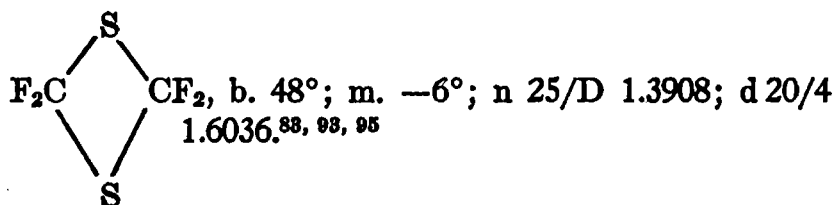
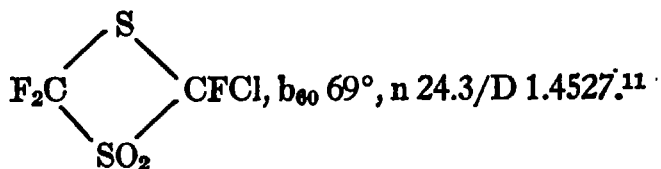
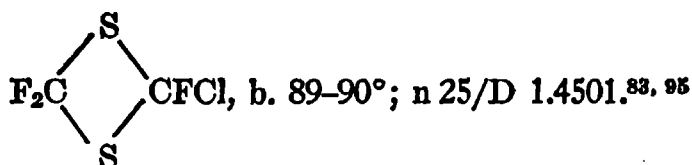
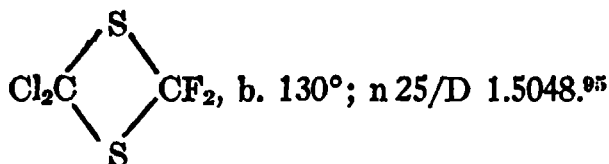
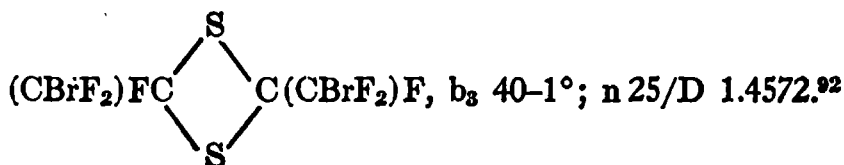
$\text{C}_9$  to  $\text{C}_{13}$



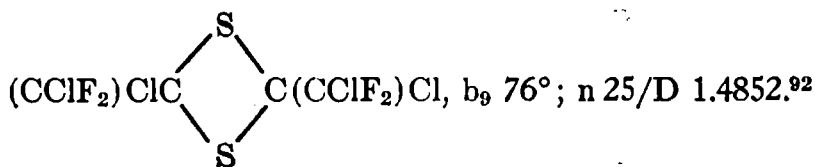
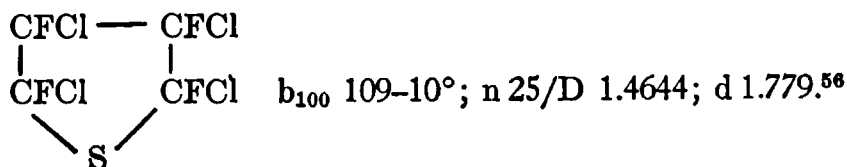
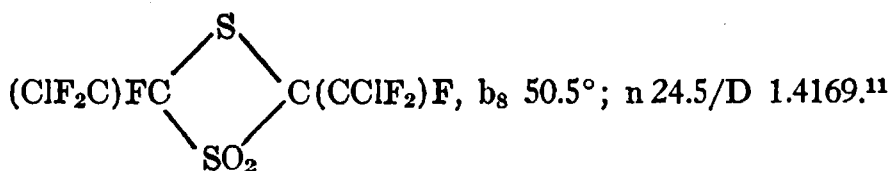
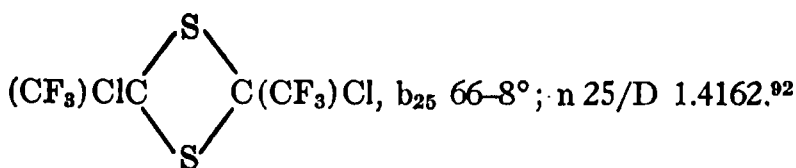
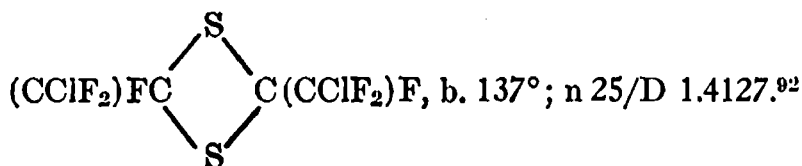
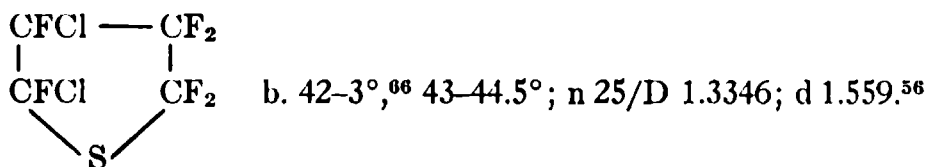
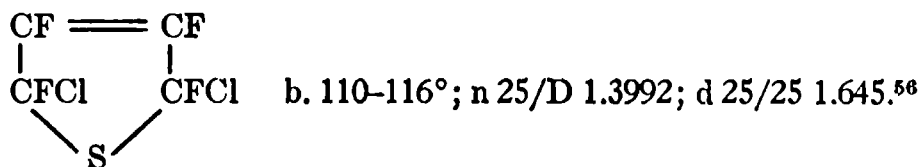
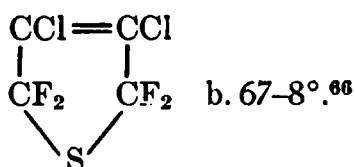
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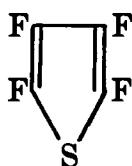
F<sub>2</sub> F<sub>2</sub>

## CYCLIC SULFIDES

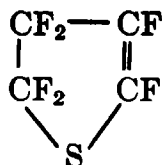
C<sub>2</sub>C<sub>4</sub>



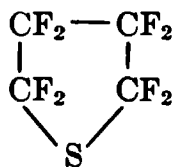




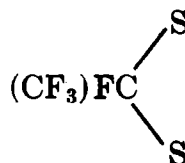
b.  $68^{\circ}$ ; n 25/D 1.3992; d 25/25 1.546.<sup>56</sup>



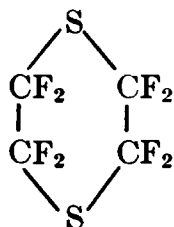
b.  $50.5^{\circ}$ ; n 25/D 1.3483.<sup>95</sup>



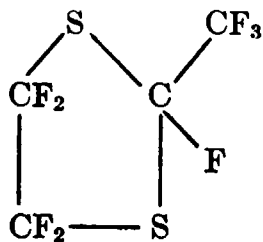
b.  $40.7^{\circ}$ ,<sup>124</sup>  $42-3^{\circ}$ ; <sup>63, 65, 70</sup> m.  $-6.5^{\circ}$ ; <sup>124</sup> n 25/D 1.3052,<sup>124</sup> 1.3050; <sup>70</sup> d 25/4 1.6339.<sup>124</sup>



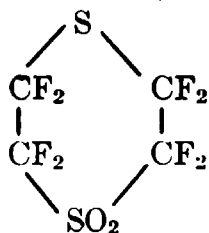
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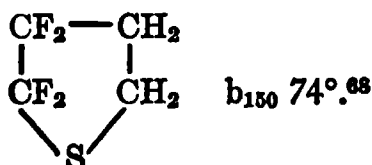
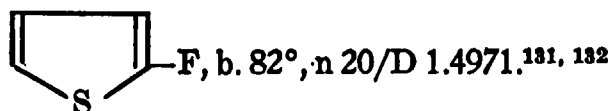
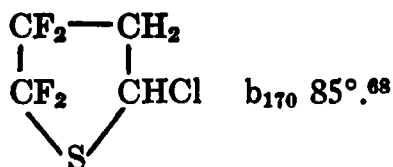
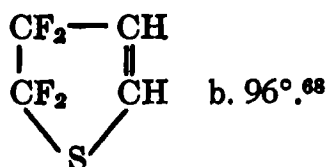
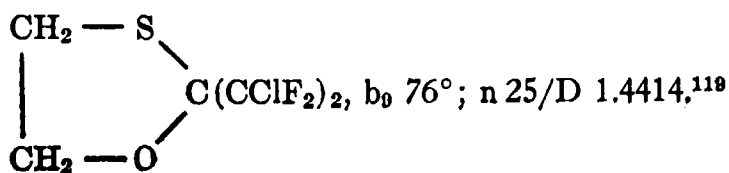
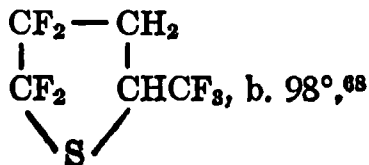
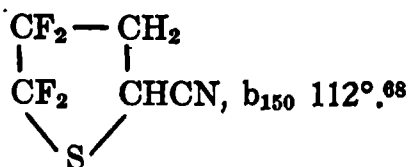
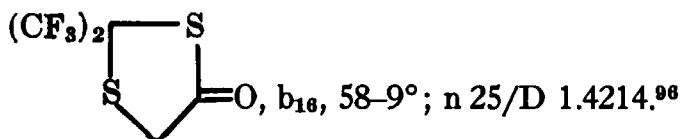
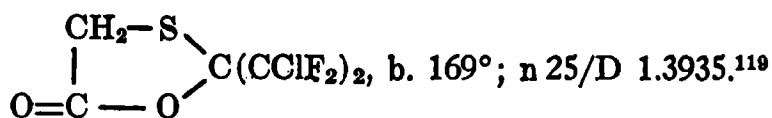
b.  $81.5^{\circ}$ ,<sup>70</sup>  $80-81^{\circ}$ ; <sup>69</sup> m.  $-6.6^{\circ}$ ; <sup>70</sup> n 25/D 1.3581.<sup>70</sup>

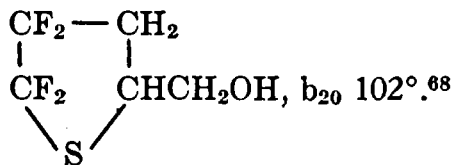
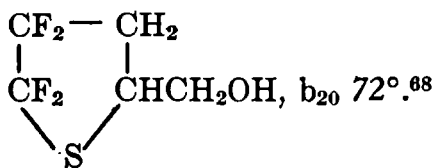
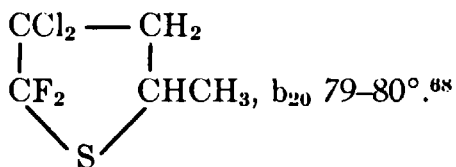
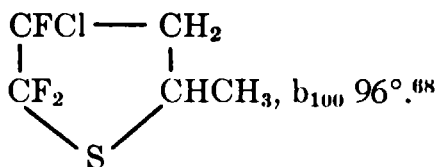
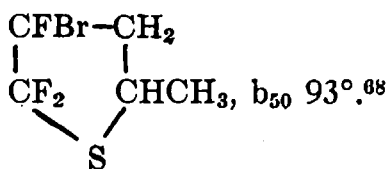
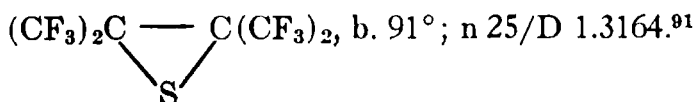
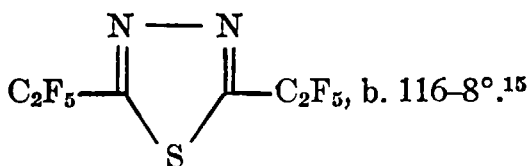
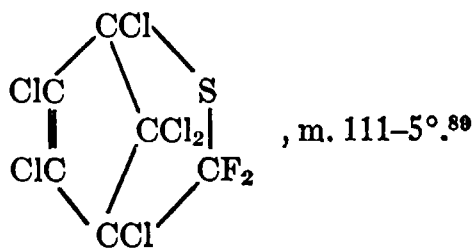


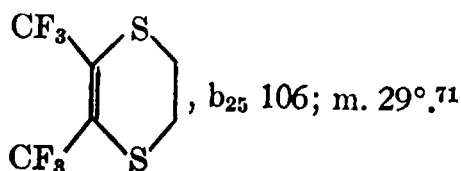
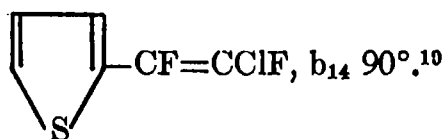
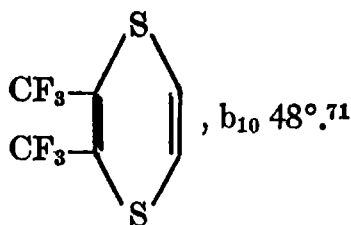
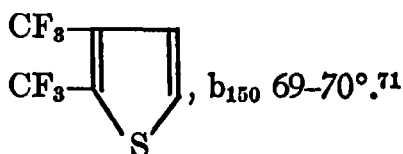
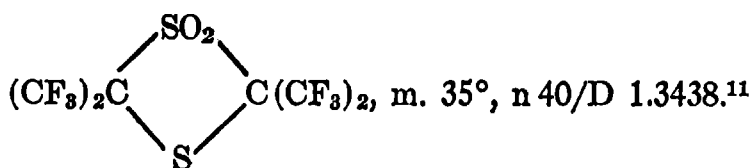
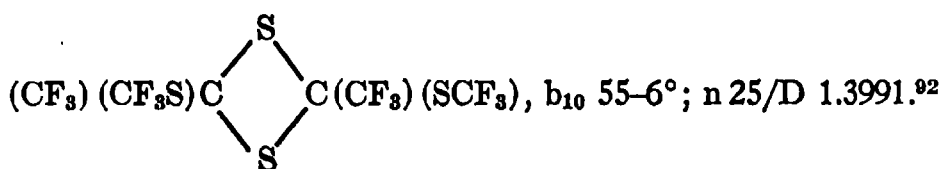
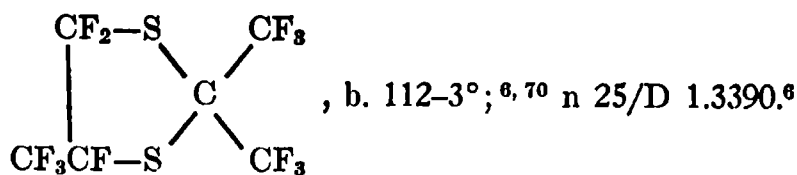
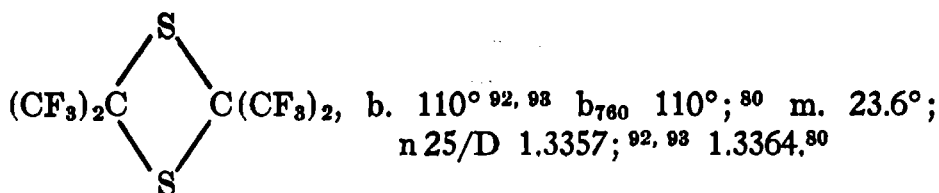
b.  $77^{\circ}$ ; m.  $-83^{\circ}$ ; n 25/D 1.3492.<sup>70</sup>

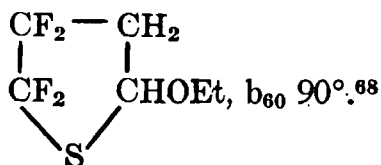
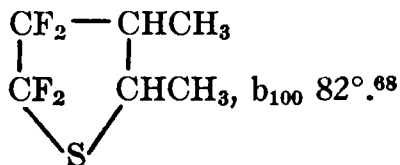
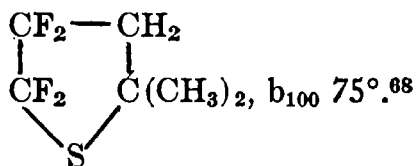
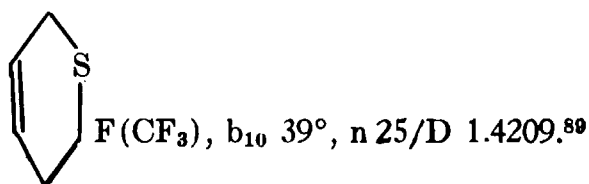
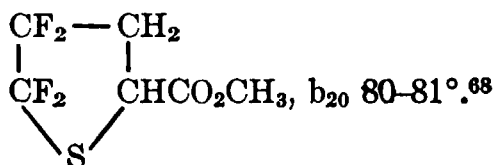
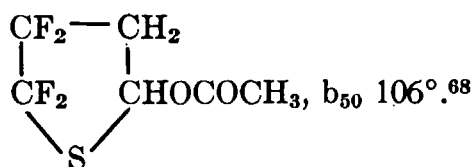
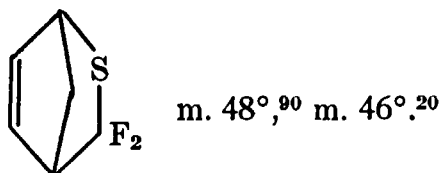
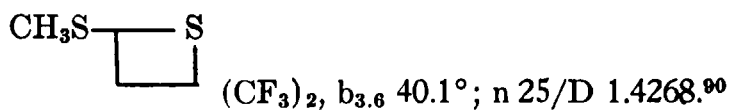
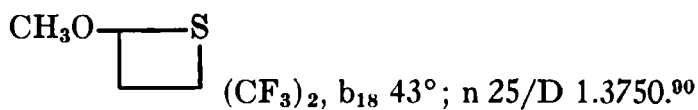


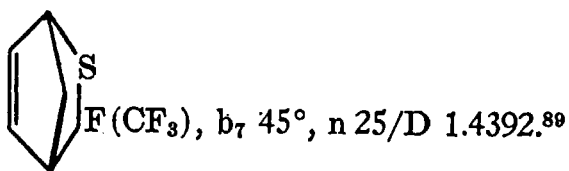
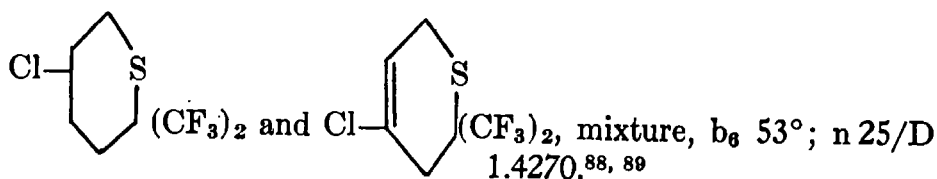
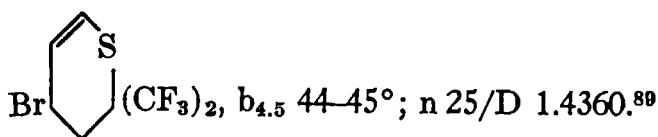
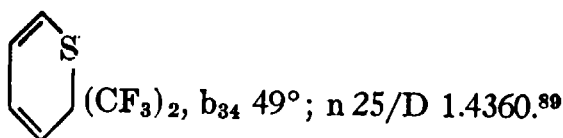
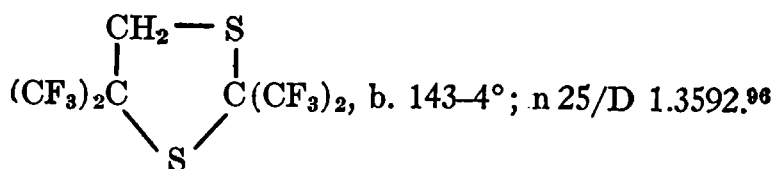
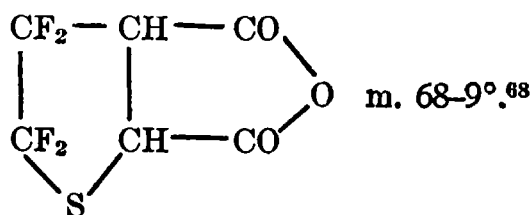
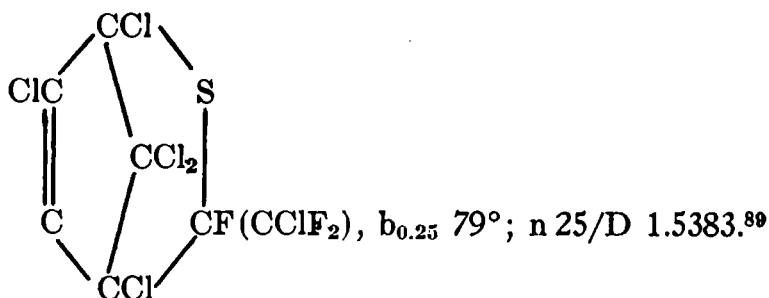
b.  $116.6^{\circ}$ , m.  $65.5-66.3^{\circ}$ .<sup>11</sup>

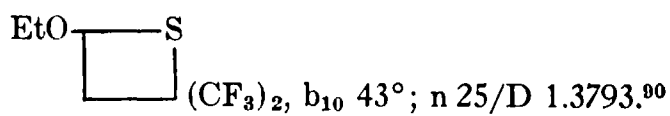
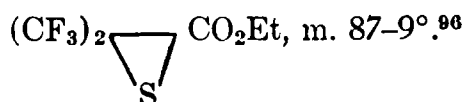
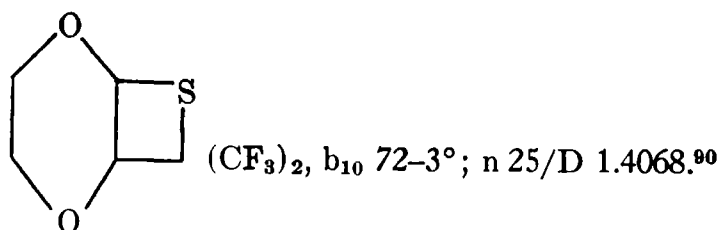
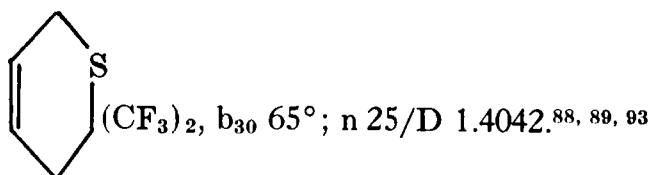
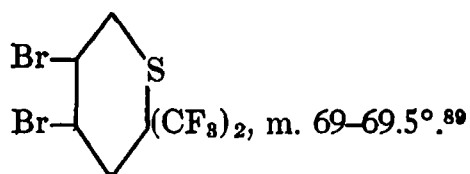
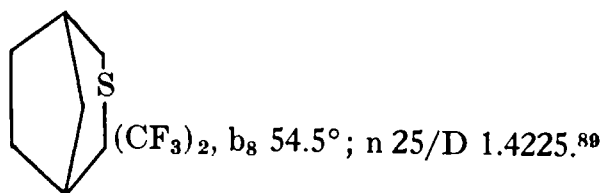
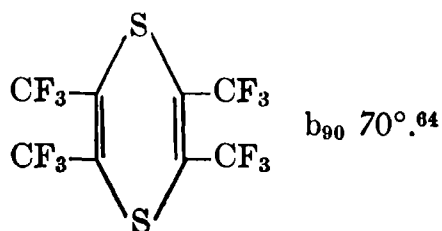
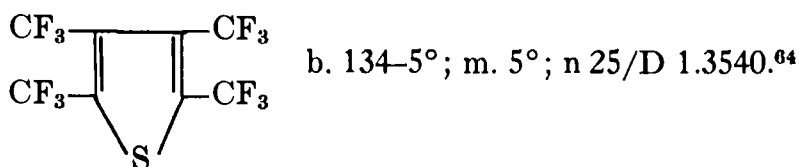
C<sub>5</sub>

C<sub>6</sub>

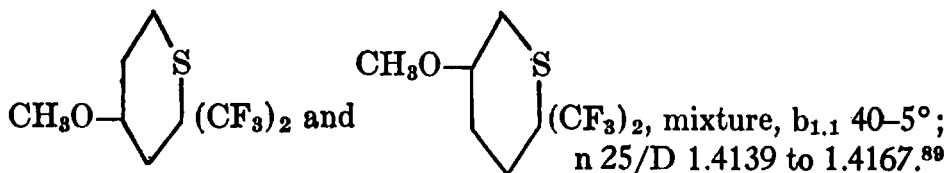
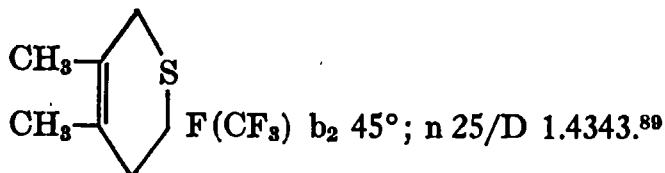
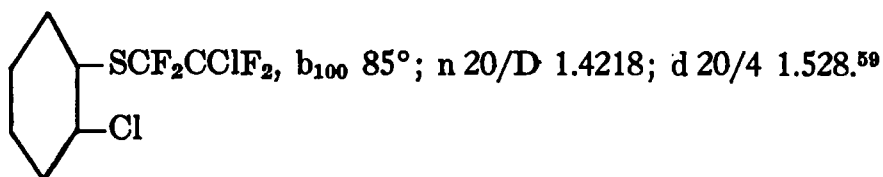
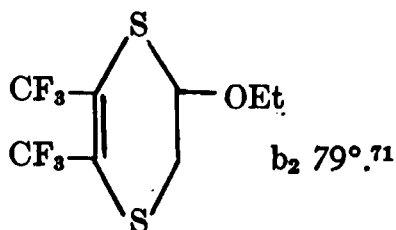
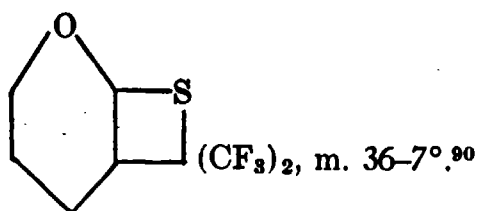
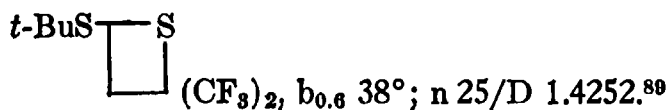
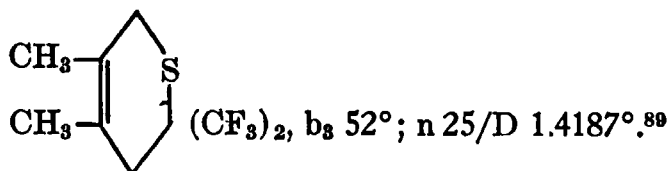


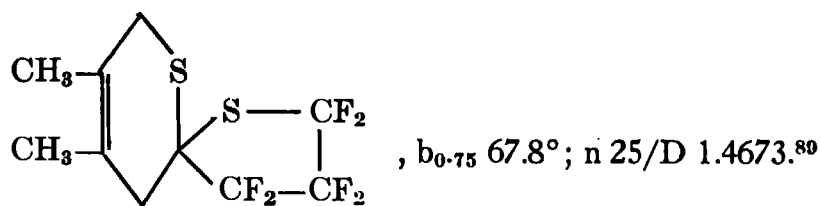
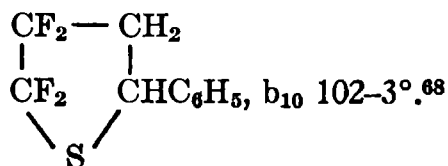
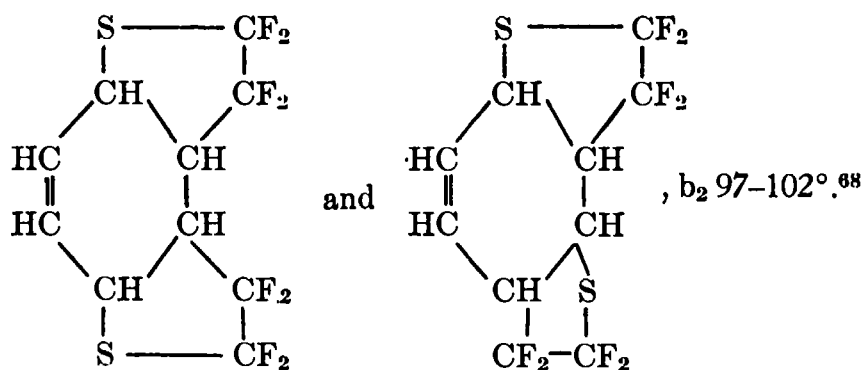
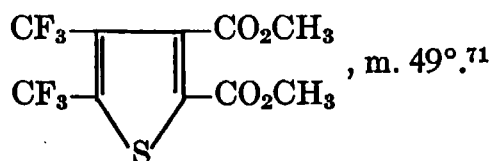
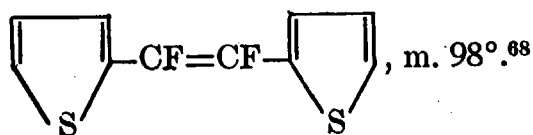
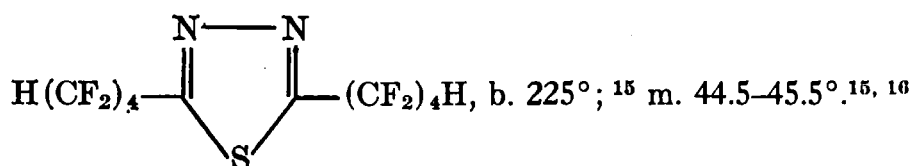
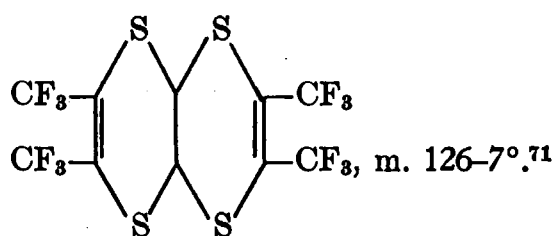


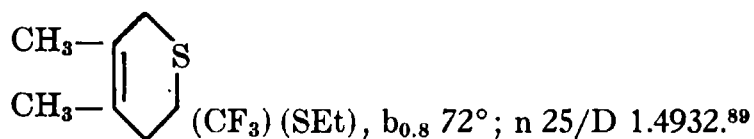
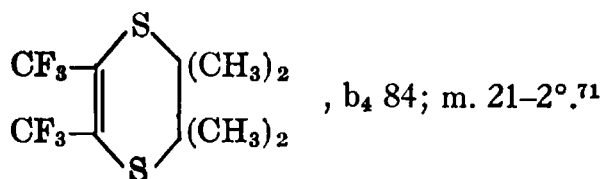
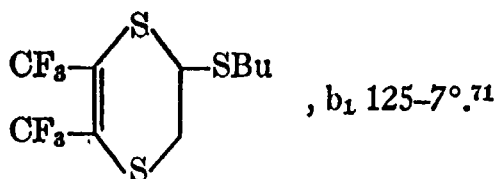
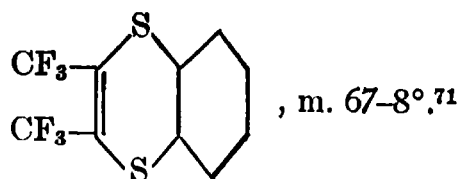
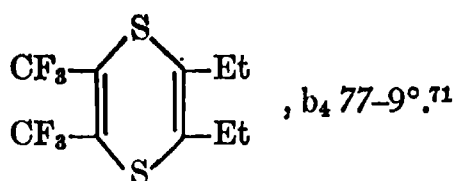
C<sub>7</sub>

C<sub>8</sub>

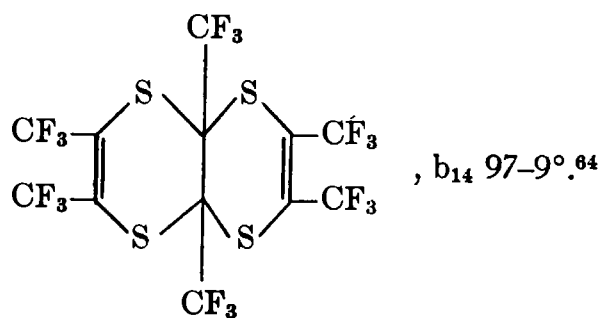
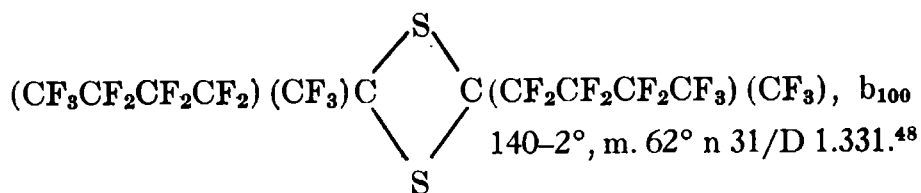


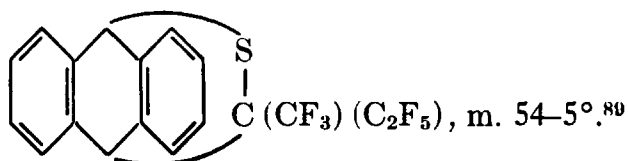
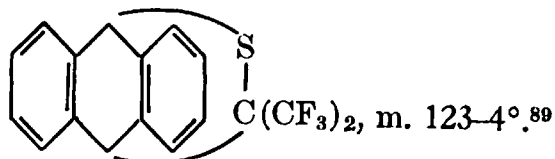
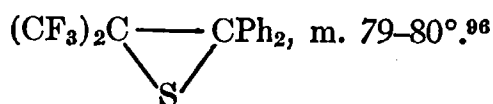
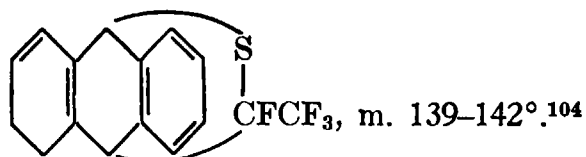
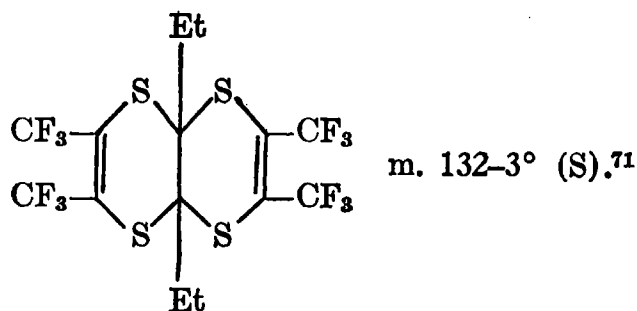
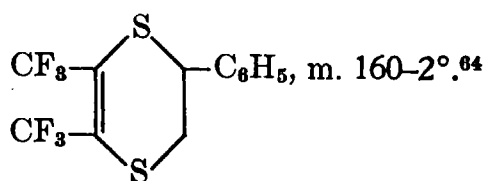
C<sub>9</sub>

C<sub>10</sub>



$\text{C}_{12}\text{--C}_{18}$





C<sub>8</sub>C<sub>9</sub>C<sub>10</sub>C<sub>12</sub>–C<sub>18</sub>

## AROMATIC SULFIDES

C<sub>7</sub>3,5-Br<sub>2</sub>,4-HOC<sub>6</sub>H<sub>2</sub>SCF<sub>3</sub>, m. 54–5°. <sup>134</sup>4-Cl,2-NO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SCF<sub>3</sub>, b<sub>17</sub> 130–4°. <sup>99</sup>2-Cl,4-NO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SCF<sub>3</sub>, b<sub>17</sub> 130–3°. <sup>99</sup>3,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SCF<sub>3</sub>, b<sub>10</sub> 82–5°. <sup>99</sup>2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SCF<sub>3</sub>, b<sub>11</sub> 82–6°. <sup>99</sup>C<sub>6</sub>F<sub>5</sub>SCCH<sub>3</sub>, b. 171–3°. <sup>110</sup>*p*-BrC<sub>6</sub>H<sub>4</sub>SCF<sub>3</sub>, b. 190–1°; n 25/D 1.5126; d 22/4 1.1413. <sup>134</sup>*p*-ClC<sub>6</sub>H<sub>4</sub>SCF<sub>3</sub>, b. 173–4°; *o*-, b<sub>15</sub> 69–72°; *m*-, b<sub>12</sub> 58–62°. <sup>99</sup>*p*-IC<sub>6</sub>H<sub>4</sub>SCF<sub>3</sub>, b<sub>10</sub> 86°; n 17/D 1.5588; d 24/4 1.8677. <sup>134</sup>*m*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SCF<sub>3</sub>, b<sub>10</sub> 103–5°. <sup>99</sup>*p*-HC<sub>6</sub>F<sub>4</sub>SCCH<sub>3</sub>, b. 169–174°. <sup>110</sup>3-NO<sub>2</sub>,4-NH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SCF<sub>3</sub>, m. 85–6°. <sup>134</sup>PhSCF<sub>3</sub>, b. 140–2°, <sup>99</sup>, <sup>134</sup> n 25/D 1.4619. <sup>134</sup>*p*-HOC<sub>6</sub>H<sub>4</sub>SCF<sub>3</sub>, b<sub>7</sub> 77–8°, m. 57–8°; *p*-nitrobenzoate, m. 81–2°. <sup>134</sup>PhSCHF<sub>2</sub>, b<sub>7</sub> 62–3°; n 25/D 1.5084; d 25/4 1.2218. <sup>52</sup>*p*-FC<sub>6</sub>H<sub>4</sub>SCCH<sub>3</sub>, b<sub>10</sub> 74°. <sup>142</sup>3,4-(NH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SCF<sub>3</sub>, m. 46–7°; diacetate, m. 190–1°. <sup>134</sup>C<sub>8</sub>3-CF<sub>3</sub>,4-NO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SCF<sub>3</sub>, b<sub>15</sub> 100–5°. <sup>99</sup>*p*-ClCOC<sub>6</sub>H<sub>4</sub>SCF<sub>3</sub>, b<sub>12</sub> 104–5°. <sup>134</sup>*p*-NCC<sub>6</sub>H<sub>4</sub>SCF<sub>3</sub>, b<sub>10</sub> 89–90°; m. 40–1°. <sup>134</sup>*m*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SCF<sub>3</sub>, b. 155°. <sup>99</sup>*m*-C<sub>6</sub>H<sub>4</sub>(SCF<sub>3</sub>)<sub>2</sub>, b<sub>18</sub> 88–93°. <sup>99</sup>PhSCF=CFCl, b. 208°; n 20/D 1.5030; d 20/4 1.387. <sup>58</sup>*p*-HOCOC<sub>6</sub>H<sub>4</sub>SCF<sub>3</sub>, m. 160–1°; <sup>134</sup> ethyl ester, b<sub>5</sub> 96–7°, n 25/D 1.4812, d 25/4 1.2752. <sup>134</sup>PhSCClFCHClF, b<sub>3</sub> 93°; n 20/D 1.540, d 20/4 1.400. <sup>58</sup>*p*-H<sub>2</sub>NCOC<sub>6</sub>H<sub>4</sub>SCF<sub>3</sub>, m. 125–6°. <sup>134</sup>PhSCF<sub>2</sub>CHF<sub>2</sub>, b<sub>72-6</sub> 104–7°, <sup>30</sup> b<sub>12</sub> 64°; <sup>58</sup> n 25/D 1.4672, <sup>30</sup> n 20/D 1.4740; d 20/4 1.3515. <sup>58</sup>

PhSCF<sub>2</sub>CH<sub>2</sub>Br, *b*<sub>14</sub> 123°; *n* 20/D 1.540; *d* 20/20 1.553.<sup>61</sup>  
 PhSCH<sub>2</sub>CClF<sub>2</sub>, *b*<sub>11</sub> 103–4°, *n* 20/D 1.5270, *d* 20/20 1.313.<sup>61</sup>  
*p*-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SCF<sub>2</sub>CHF<sub>2</sub>, *b*<sub>3</sub> 80–3°, *n* 25/D 1.5138.<sup>30</sup>  
*o*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SCH<sub>3</sub>, *b*<sub>743</sub> 192–3°, *b*<sub>25</sub> 91°; *n* 25/D 1.497; *d* 20/4 1.270; *m*-, *b*<sub>743</sub> 208–9°, *b*<sub>25</sub> 96°; *m*. 3.7–5°; *n* 25/D 1.509, *d* 25/4 1.308; *p*-, *b*. 198.5–199°, *b*<sub>20</sub> 80°; *m*. 37°.<sup>81</sup>

C<sub>9</sub>

2,4-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SCH<sub>3</sub>, *b*. 204–5°, *b*<sub>12</sub> 88.5°; *m*. 20.3–21.7°; *n* 25/D 1.464; *d* 25/4 1.453.<sup>81</sup>  
 2,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SCH<sub>3</sub>, *b*. 195–6°, *b*<sub>10</sub> 74°; *m*. 17–18.5°; *n* 25/D 1.458; *d* 25/4 1.445.<sup>81</sup>  
 2,6-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SCH<sub>3</sub>, *b*. 205–6°, *b*<sub>12</sub> 67°; *m*. 20.4–22.0; *n* 25/D 1.464; *d* 25/4 1.453.<sup>81</sup>  
 3-NO<sub>2</sub>,4-AcNHC<sub>6</sub>H<sub>3</sub>SCF<sub>3</sub>, *m*. 101–2°.<sup>134</sup>  
*m*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>CO<sub>2</sub>H, *b*<sub>2</sub> 140–3°; ethyl ester, *b*<sub>1</sub> 100–1°.<sup>122</sup>

C<sub>10</sub>–C<sub>12</sub>

2,4(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SCH<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>, *m*. 77–77.5°.<sup>41</sup>  
*p*-HC<sub>6</sub>H<sub>4</sub>SPh, *b*<sub>760</sub> 265°, *b*<sub>1.5</sub> 117°.<sup>110</sup>  
 (FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>S, *o*-, *b*<sub>12</sub> 165–6°; *m*-, *b*<sub>10</sub> 140–1°; *p*-, *b*<sub>7</sub> 133–5°,<sup>101</sup> *b*<sub>9</sub> 136–7°.<sup>74</sup>  
*o*-FC<sub>6</sub>H<sub>4</sub>SPh, *b*<sub>15</sub> 131–2°; *m*-, *b*<sub>13</sub> 128–9°; *p*-, *b*<sub>17</sub> 149–50°,<sup>101</sup> *b*<sub>11</sub> 141–2°, *b*<sub>15</sub> 147–8°.<sup>74</sup>  
 2,4,6-(CF<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>S-*i*-Pr, *b*. 212–3°, *b*<sub>3</sub> 63°; *n* 25/D 1.428; *d* 25/4 1.437.<sup>81</sup>

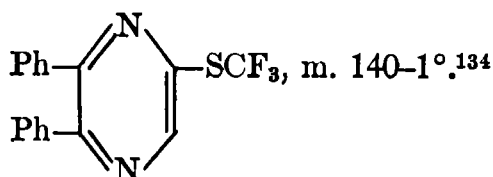
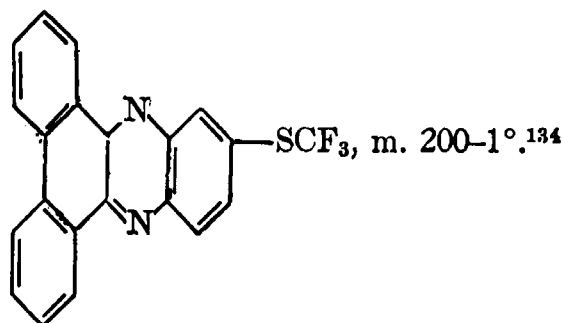
C<sub>13</sub>–C<sub>14</sub>

4-CF<sub>3</sub>,2NO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-4, *m*. 129–130°.<sup>121</sup>  
 2-CF<sub>3</sub>,4NO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-4, *m*. 162.5–163.5°.<sup>121</sup>  
*m*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SC<sub>6</sub>H<sub>4</sub>Cl-*p*, *b*<sub>1</sub> 118–121°.<sup>10</sup>  
 2-CF<sub>3</sub>,4NO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SPh, *m*. 11°.<sup>101</sup>  
 4-CF<sub>3</sub>,2NO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SPh, *m*. 73°,<sup>101</sup> 72.5–73.5°.<sup>121</sup>  
*m*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SPh, *b*<sub>15</sub> 159–60°,<sup>101</sup> *b*<sub>12–14</sub> 146–158°.<sup>10</sup>  
 4-FC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>F-4,<sup>1</sup> *m*. 46°.<sup>101</sup>  
*p*-FC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>Ph, *m*. 34°.<sup>101</sup>  
*p*-FC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SPh, *m*. 65°.<sup>101</sup>  
 (4-CF<sub>3</sub>,2NO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>S, *m*. 146°,<sup>101</sup> 142–3°,<sup>111</sup> 144–5°.<sup>121</sup>  
 (2-CF<sub>3</sub>,4NO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>S, *m*. 137°,<sup>101</sup> 136–7°.<sup>121</sup>  
 (*m*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>S, *b*<sub>1</sub> 101–2°,<sup>101</sup> *b*<sub>0.8</sub> 93–100°.<sup>10</sup>  
 (4-CF<sub>3</sub>,2NH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>S, *m*. 89–90°.<sup>111</sup>

$m$ -CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>- $p$ ,  $b_{1.5}$  115°; - $m$ ,  $b_{0.6}$  99–110°; - $o$ ,  $b_{0.5}$  94–95°. <sup>10</sup>

C<sub>17</sub>—C<sub>21</sub>

$m$ -CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SC<sub>6</sub>H<sub>4</sub>( $t$ -Bu)- $p$ ,  $b_{0.7}$  119–123°. <sup>10</sup>



2,4,6-(CF<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>SC<sub>12</sub>H<sub>25</sub>, m. 41°. <sup>81</sup>

#### ACYCLIC DISULFIDES AND POLYSULFIDES

C<sub>2</sub>

(CCl<sub>2</sub>F)<sub>2</sub>S<sub>2</sub>,  $b_{36}$  103;  $n_{25/D}$  1.5155. <sup>116</sup>

CCl<sub>3</sub>S<sub>2</sub>CF<sub>3</sub>,  $b_{60}$  74;  $n_{25/D}$  1.4739. <sup>78</sup>

(CF<sub>3</sub>)<sub>2</sub>S<sub>2</sub>,  $b$ , 34°, <sup>44, 128</sup>, 34.5, <sup>2</sup>  $b_{760}$  34.6°. <sup>5</sup>

(CF<sub>3</sub>)<sub>2</sub>S<sub>3</sub>,  $b$ , 86.4°;  $n_{20/D}$  1.4032. <sup>44</sup>

(CF<sub>3</sub>)<sub>2</sub>S<sub>4</sub>,  $b$ , 135°;  $n_{20/D}$  1.4608. <sup>44</sup>

C<sub>3</sub>

EtS<sub>2</sub>CF<sub>3</sub>,  $b$ , 82° (extrap.). <sup>28</sup>

C<sub>4</sub>

(CClF<sub>2</sub>CF<sub>2</sub>)<sub>2</sub>S<sub>2</sub>,  $b$ , 141°, <sup>136</sup> 139–40°; <sup>59</sup> 141–2°; <sup>105</sup>  $n_{20/D}$  1.3970, <sup>59</sup>  $n_{21/D}$  1.3915; <sup>136</sup>  $d_{20/20}$  1.685, <sup>59</sup>  $d_{21/4}$  1.6810. <sup>136</sup>

(CClF<sub>2</sub>CF<sub>2</sub>)<sub>2</sub>S<sub>3</sub>,  $b_5$  50–2°;  $n_{20/D}$  1.4340;  $d_{20/20}$  1.707. <sup>59</sup>

(CF<sub>3</sub>CF<sub>2</sub>)<sub>2</sub>S<sub>2</sub>,  $b$ , 78–9°;  $n_{23/D}$  1.3225. <sup>86</sup>

CF<sub>3</sub>CH(SCF<sub>3</sub>)(SSCF<sub>3</sub>),  $b$ , 118–9°;  $n_{25/D}$  1.3752. <sup>96</sup>

(CHClFCF<sub>2</sub>)<sub>2</sub>S<sub>2</sub>,  $b_2$  70°, <sup>34</sup>  $b_{12}$  71–2°; <sup>43</sup>  $n_{0/D}$  1.4910, <sup>34</sup>  $n_{25/D}$  1.4329; <sup>43</sup>  $d_{0/4}$  1.7496. <sup>34</sup>

(CClF<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>S<sub>3</sub>,  $b_7$  93–5°;  $n_{20/D}$  1.494;  $d_{20/20}$  1.588. <sup>61</sup>

$(\text{CF}_3\text{CH}_2)_2\text{S}_2$ , b.  $130-1^\circ$ ,<sup>41</sup> b.  $130-180^\circ$ ; <sup>1.5</sup> n 25/D 1.3890.<sup>41</sup>

$(\text{CF}_3\text{CH}_2)_2\text{S}_3$ , b.  $180-200^\circ$ .<sup>1.5</sup>

$(\text{CHF}_2\text{CH}_2)_2\text{S}_2$ ,  $b_{21}$  84; n 24/D 1.4465.<sup>43</sup>

$\text{C}_8$

$(\text{CF}_3\text{CF}_2\text{CF}_2)_2\text{S}_2$ , b.  $123^\circ$ ,<sup>125</sup>  $122.2^\circ$ ,<sup>50</sup>  $122^\circ$ ; <sup>47</sup> n 25/D 1.3231,<sup>125</sup>  
n 28/D 1.3222; <sup>50</sup> d 20/4 1.6940.<sup>50</sup>

$[(\text{CF}_3)_2\text{CF}]_2\text{S}_2$ ,  $b_{773}$   $119.0^\circ$ ,<sup>14</sup> b.  $121-3^\circ$ ; <sup>95</sup> n 20/D 1.32614.<sup>14</sup>

$(\text{CF}_3\text{CF}_2\text{CF}_2)_2\text{S}_3$ , b.  $155.5^\circ$ ,<sup>125</sup>  $153^\circ$ ; <sup>50</sup> n 25/D 1.3594,<sup>115</sup> n 31/D  
1.3600; d 31/4 1.6984.<sup>50</sup>

$[(\text{CF}_3)_2\text{CF}]_2\text{S}_3$ ,  $b_{764}$   $150.0^\circ$ ,<sup>14</sup> b.  $150-5^\circ$ ; <sup>95</sup> n 20/D 1.36092.<sup>14</sup>

$[(\text{CF}_3)_2\text{CF}]_2\text{S}_4$ , b.  $180-186^\circ$ .<sup>95</sup>

$(\text{CF}_3)_2\text{CHS}_2\text{C}(\text{CF}_3)_2\text{Br}$ ,  $b_{13}$   $49-50^\circ$ ; n 25/D 1.3752.<sup>96</sup>

$(\text{CF}_3)_2\text{CHS}_2\text{C}(\text{CF}_3)_2\text{Cl}$ ,  $b_{48}$   $67^\circ$ ; n 25/D 1.3598.<sup>93</sup>

$[(\text{CClF}_2)_2\text{CH}]_2\text{S}_2$ ,  $b_{0.7}$   $54-57^\circ$ ; n 25/D 1.4367.<sup>41</sup>

$[(\text{CF}_3)_2\text{CH}]_2\text{S}_2$ , b.  $124^\circ$ ; n 25/D 1.3380.<sup>96</sup>

$(\text{CF}_3)_2\text{CHSC}(\text{CF}_3)_2\text{OH}$ ,  $b_{38}$   $60^\circ$ ; n 25/D 1.3514.<sup>96</sup>

$\text{CHF}_2\text{CF}_2\text{SCH}(\text{CHF}_2)\text{SSCF}_2\text{CHF}_2$ ,  $b_{0.8}$   $50-1^\circ$ ; n 25/D 1.4151.<sup>96</sup>

$\text{C}_8$

$[(\text{CF}_3)_2\text{C}=\text{C}(\text{CF}_3)]_2\text{S}_2$ ,  $b_{25}$   $82^\circ$ .<sup>64</sup>

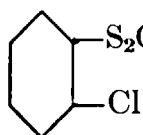
$[(\text{CF}_3)_2\text{C}=\text{C}(\text{CF}_3)]_2\text{S}_3$ ,  $b_8$   $88-9^\circ$ .<sup>64</sup>

$[(\text{C}_2\text{F}_5)(\text{CF}_3)\text{CF}]_2\text{S}_2$ ,  $b_{10}$   $43-6^\circ$ ; n 26.3/D 1.3293.<sup>54</sup>

$[(\text{C}_2\text{F}_5)(\text{CF}_3)\text{CF}]_2\text{S}_3$ ,  $b_{10}$   $70-1^\circ$ ; n 26.3/D 1.3618.<sup>54</sup>

2,4- $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{S}_2\text{CH}_2\text{CF}_3$ , m.  $64.5-65^\circ$ .<sup>41</sup>

$\text{PhNHCOS}_2\text{CCl}_2\text{F}$ , m.  $95-6^\circ$ .<sup>117</sup>



$b_{18}$   $136-7^\circ$ ; n 20/D 1.4912; d 20/20 1.458.<sup>59</sup>

$\text{C}_9\text{--C}_{11}$

2,4- $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{S}_2\text{CH}_2\text{CF}_2\text{CF}_3$ , m.  $65-6^\circ$ .<sup>41</sup>

2,4- $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{S}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_3$ , m.  $75-75.5^\circ$ .<sup>41</sup>

$[\text{H}(\text{CF}_2)_4\text{CH}_2]_2\text{S}_2$ ,  $b_{0.5}$   $84^\circ$ ; n 25/D 1.3688.<sup>41</sup>

$[\text{H}(\text{CF}_2)_4\text{CH}_2]_2\text{S}_3$ ,  $b_2$   $144^\circ$ ; n 25/D 1.3972.<sup>41</sup>

2,4- $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{S}_2\text{CH}(\text{C}_2\text{F}_5)_2$ , m.  $72-3^\circ$ .<sup>41</sup>

2,4- $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{S}_2\text{CH}_2(\text{CF}_2)_4\text{H}$ , m.  $55.5-56.5^\circ$ .<sup>41</sup>

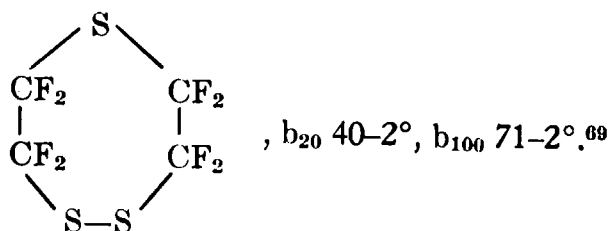
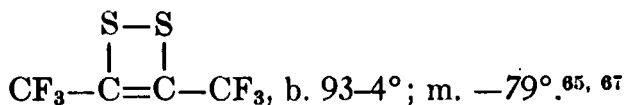
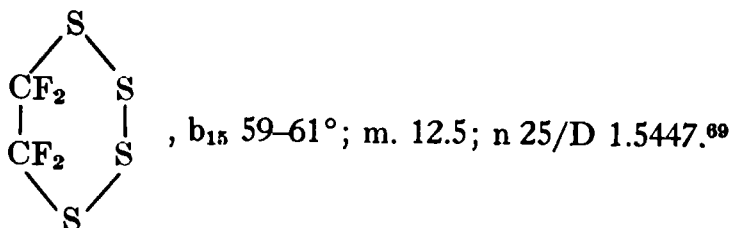
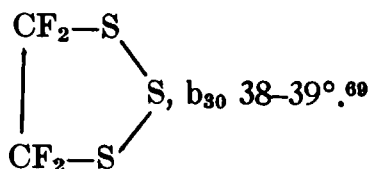
$\text{C}_{12}\text{--C}_{20}$

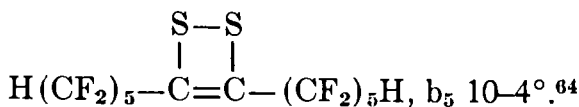
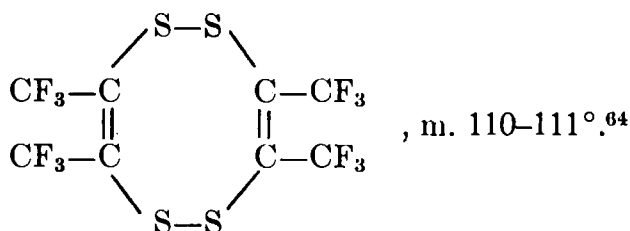
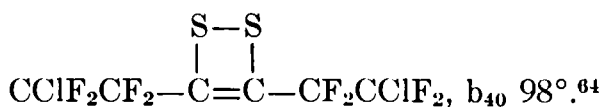
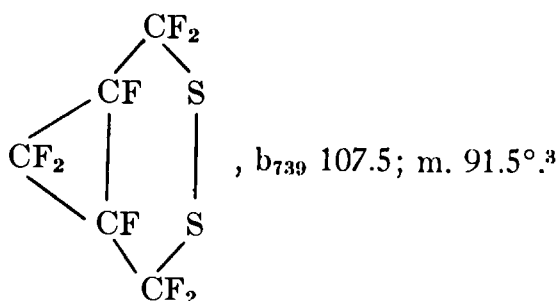
$(\text{C}_6\text{F}_5)_2\text{S}_2$ , m.  $50-1^\circ$ .<sup>110</sup>



- $[(n\text{-C}_4\text{F}_9)(\text{CF}_3)\text{CF}]_2\text{S}_2$ ,  $b_8$   $94^\circ$ ;  $n$  23/D 1.3300°. <sup>49</sup>  
 $[(n\text{-C}_4\text{F}_9)(\text{CF}_3)\text{CF}]_2\text{S}_3$ ,  $b$   $<0.1$   $66^\circ$ ;  $n$  28.8/D 1.3469°. <sup>49</sup>  
 $[(n\text{-C}_4\text{F}_9)(\text{CF}_3)\text{CF}]_2\text{S}_4$ ,  $b$   $<0.1$   $80^\circ$ ;  $n$  20/D 1.3791°. <sup>49</sup>  
 $[(n\text{-C}_4\text{F}_9)(\text{CF}_3)\text{CF}]_2\text{S}_5$ ,  $n$  19.5/D 1.3975°. <sup>49</sup>  
 $(p\text{-HC}_6\text{F}_4)_2\text{S}_2$ ,  $m$ .  $38^\circ$ . <sup>110</sup>  
 $(3,4\text{-F}_2,2\text{-NO}_2\text{C}_6\text{H}_2)_2\text{S}_2$ ,  $m$ .  $109\text{--}11^\circ$ . <sup>111</sup>  
 $(2\text{-F},4\text{-NO}_2\text{C}_6\text{H}_3)_2\text{S}_2$ ,  $m$ .  $143\text{--}144^\circ$ . <sup>111</sup>  
 $(p\text{-FC}_6\text{H}_4)_2\text{S}_2$ ,  $b_{10}$   $170\text{--}171^\circ$ . <sup>101</sup>  
 $(3,4\text{-F}_2,2\text{NH}_2\text{C}_6\text{H}_2)_2\text{S}_2$ ,  $m$ .  $119\text{--}120^\circ$ . <sup>111</sup>  
 $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{S}_2\text{CH}(n\text{-C}_3\text{F}_7)_2$ ,  $m$ .  $99\text{--}100^\circ$ . <sup>41</sup>  
 $(4\text{-CF}_3,2\text{NO}_2\text{C}_6\text{H}_3)_2\text{S}_2$ ,  $m$ .  $155^\circ$ , <sup>101</sup>  $158\text{--}161^\circ$ , <sup>53</sup>  $152\text{--}4^\circ$ . <sup>9</sup>  
 $(2\text{-CF}_3)_4\text{NO}_2\text{C}_6\text{H}_3)_2\text{S}_2$ ,  $m$ .  $156^\circ$ . <sup>101</sup>  
 $[\text{H}(\text{CF}_2)_6\text{CH}_2]_2\text{S}_2$ ,  $b_{20}$   $165\text{--}175^\circ$ . <sup>31</sup>  
 $(p\text{-FC}_6\text{H}_4\text{CH}_2)_2\text{S}_2$ ,  $m$ .  $65^\circ$ . <sup>101</sup>  
 $(2\text{-CF}_3,4\text{NH}_2\text{C}_6\text{H}_3)_2\text{S}_2$ ,  $m$ .  $73\text{--}4^\circ$ . <sup>9</sup>  
 $(1\text{-FC}_{10}\text{H}_6)_2\text{S}_2$ ,  $m$ .  $175^\circ$ . <sup>101</sup>

## CYCLIC DISULFIDES AND POLYSULFIDES





## SULFENYL HALIDES

 $C_1$ 

$CF_3SBr$ , b.  $36^\circ$ ; n 16/D 1.3855; d 16/16 1.7704.<sup>140</sup>

$CBrClFSBr$ , b.  $134^\circ$ ; n 18/D 1.5616; d 18/4 2.3676.<sup>140</sup>

$CBrF_2SBr$ , b.  $107^\circ$ ; n 17/D 1.5210; d 17/4 2.3550.<sup>140</sup>

$CF_3SCl$ , b.  $0^\circ$ ,<sup>139</sup>  $-0.7^\circ$ ,<sup>44</sup>  $-1^\circ$ .<sup>127, 128</sup>

$CClF_2SCl$ , b.  $52^\circ$ ,<sup>138</sup>  $50^\circ$ ,<sup>4</sup>  $b_{27}$   $0^\circ$ ,<sup>20</sup> n 19/D 1.4195,<sup>138</sup> n 20/D 1.4136;<sup>4</sup> d 19/19 1.5344.<sup>138</sup>

$CCl_2FSCl$ , b.  $97-8^\circ$ ; n 25/D 1.4767.<sup>116</sup>

 $C_2$ 

$CClF_2CF_2SCl$ , b.  $65^\circ$ ; n 20/D 1.3890; d 20/4 1.605.<sup>59</sup>

$CClF_2CF_2S_2Cl$ , b.  $126^\circ$ ; n 20/D 1.4112; d 20/4 1.674.<sup>59</sup>

$CHClFCF_2SCl$ , b.  $98^\circ$ ; n 25/D 1.4153.<sup>39, 43</sup>

$CHF_2CF_2SCl$ , b.  $57-9^\circ$ ; n 25/D 1.3610.<sup>39, 43</sup>

$CClF_2CH_2SCl$ , b.  $110-112^\circ$ ; n 25/D 1.448; d 20/20 1.523.<sup>34</sup>

$C_3$ 

$(CF_3)_2CBrSBr$ ,  $b_{38}$  48–9°;  $n_{25/D}$  1.4368.<sup>96</sup>

$(CF_3)_2CClSCl$ ,  $b$ , 89–90°;  $n_{25/D}$  1.3706.<sup>96</sup>

$CF_3CF_2CF_2SCl$ ,  $b$ , 51–51.5°;  $n_{23/D}$  1.3239.<sup>62</sup>

$(CF_3)_2CFSCl$ ,  $b$ , 54–5°.<sup>1</sup>

$(CF_3)_2CFSF$ ,  $b$ , <0°, pale green liquid,  $F^{19}$  NMR + 293 p.p.m. displaced from Freon 112.<sup>112</sup>

$CF_3CF_2CF_2SF?$ ,  $b$ , –15–0°.<sup>62</sup>

 $C_5$ – $C_8$ 

$H(CF_2)_4CH_2SCl$ ,  $b_6$  44°,  $n_{24/D}$  1.3700.<sup>41</sup>

$EtSC(CF_3)_2SCl$ ,  $b_4$  41–2°;  $n_{25/D}$  1.4464.<sup>96</sup>

$n$ - $C_4F_9CF(CF_3)SCl$ ,  $b_{97}$  63–63.8°;  $n_{26/D}$  1.3237.<sup>49</sup>

## ISOTHIOCYANATES AND THIOCYANATES

$CCl_2FSCN$ ,  $b_{80}$  59°;  $n_{18/D}$  1.4661;  $d_{18/18}$  1.5355.<sup>137</sup>

$CClF_2SCN$ ,  $b$ , 85°;  $n_{15/D}$  1.4050;  $d_{15/15}$  1.4221.<sup>137</sup>

$CF_3SCN$ ,  $b$ , 36°;  $m$ , –70°; Trouton's constant 24.8.<sup>25.5</sup>

$CF_3SSCN$ ,  $m$ , –35.5°; dec. room temp.<sup>25.5</sup>

$CClF_2CF_2SCN$ ,  $b$ , 98°;  $n_{16/D}$  1.3792;  $d_{16/16}$  1.4769.<sup>137</sup>

$CF_3COSCNCN$ ,  $b$ , 72–4°;  $n_{25/D}$  1.369.<sup>102</sup>

$CHF_2COSCNCN$ ,  $b_{50}$  76°;  $n_{20/D}$  1.5327;  $d_{20/4}$  1.3527.<sup>108</sup>

$CHClFCH_2SCN$ ,  $b_{25}$  97°;  $n_{21/D}$  1.4875;  $d_{21/21}$  1.3982.<sup>137</sup>

$CHF_2CH_2SCN$ ,  $b_{80}$  96°;  $n_{18/D}$  1.4442;  $d_{18/18}$  1.3434.<sup>137</sup>

$CHF_2CH_2NCS$ ,  $b_{100}$  76°;  $n_{25/D}$  1.4725;  $d_{25/25}$  1.3274.<sup>137</sup>

$F(CH_2)_2SCN$ ,  $b_{20}$  67–9°,<sup>55</sup>  $b_{19}$  77.5–78.5; <sup>114</sup>  $n_{25/D}$  1.4615.<sup>55</sup>

$CF_3CF_2COSCNCN$ ,  $b$ , 87°;  $d_{25/4}$  1.503.<sup>102</sup>

$F(CH_2)_3SCN$ ,  $b_{10}$  78–9°;  $n_{25/D}$  1.4591.<sup>55</sup>

$CF_3CF_2CF_2COSCNCN$ ,  $b$ , 106°;  $d_{25/4}$  1.644.<sup>102</sup>

$F(CH_2)_4SCN$ ,  $b_{13}$  97–8°;  $n_{25/D}$  1.4610.<sup>55</sup>

$p$ - $FC_6H_4SCN$ ,  $b$ , 230–2°.<sup>101</sup>

$p$ - $FC_6H_4NCS$ ,  $b$ , 227–8°;  $m$ -,  $b$ , 226–7°;  $m$ , 12°.<sup>101</sup>

$F(CH_2)_6SCN$ ,  $b_{11}$  124–5°;  $n_{25/D}$  1.4595.<sup>55</sup>

## SULFUR ATTACHED TO OTHER ELEMENTS

*Arsenic*

$CF_3SAsCl_2$ ,  $b$ , 125°;  $m$ , –34°.<sup>29</sup>

$(CF_3S)_2AsCl$ ,  $b$ , 128°;  $m$ , –50°.<sup>29</sup>

*Nitrogen*

$CF_3SNH_2$ ,  $b$ , 46.5° (extrap.);  $m$ , –89°.<sup>28</sup>

$\text{CF}_3\text{SNCO}$ , b.  $27^\circ$ ; m.  $-97^\circ$ ; Trouton's constant 21.2.<sup>25.5</sup>

$(\text{CF}_3)_2\text{NSCl}$ , b.  $49.5-51^\circ$ .<sup>127</sup>

$(\text{CF}_3\text{S})_2\text{NH}$ , b.  $73^\circ$  (extrap.), m.  $-47^\circ$ .<sup>28</sup>

$\text{CF}_3\text{SNHCONH}_2$ , m.  $102-4^\circ$ .<sup>25.5</sup>

$\text{CF}_3\text{SNHCH}_3$ , b.  $47^\circ$  (extrap.).<sup>28</sup>

$(\text{CF}_3\text{SNH})_2\text{CO}$ , m.  $182^\circ$ .<sup>25.5</sup>

$(\text{CF}_3\text{S})_2\text{NCONH}_2$ , m.  $43^\circ$ .<sup>25.5</sup>

$\text{CF}_3\text{SNHCONHCH}_3$ , m.  $140^\circ$  (sublimes).<sup>25.5</sup>

$[(\text{CF}_3)_2\text{N}]_2\text{S}$ , b.  $75^\circ$ ; <sup>141</sup> 76-7; <sup>127</sup> n 25/D 1.2879; d 25/4 1.705.<sup>141</sup>

$[(\text{CF}_3)_2\text{N}]_2\text{S}_2$ , b.  $104^\circ$ ; <sup>141</sup> 99-101; <sup>127</sup> n 25/D 1.3016; d 25/4 1.701.<sup>141</sup>

$\text{CF}_3\text{SNHCON}(\text{CH}_3)_2$ , m.  $126^\circ$ .<sup>25.5</sup>



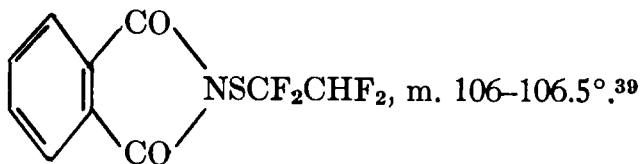
$\text{CClF}_2\text{CF}_2\text{SNet}_2$ , b<sub>60</sub>  $66-7^\circ$ ; n 20/D 1.4850; d 20/20 1.341.<sup>59</sup>

$\text{CClF}_2\text{CH}_2\text{SNet}_2$ , b<sub>7</sub>  $52-4^\circ$ ; n 20/D 1.437; d 20/20 1.169.<sup>61</sup>

$\text{CF}_3\text{SNHPh}$ , b.  $191^\circ$  (extrap.).<sup>28</sup>

$\text{CF}_3\text{SNHCONHPh}$ , m.  $179^\circ$ .<sup>25.5</sup>

$\text{CF}_3\text{SNHCONPh}_2$ , m.  $157^\circ$ .<sup>25.5</sup>



### Oxygen

$\text{CF}_3\text{SOCH}_3$ , b.  $25-6^\circ$ .<sup>1</sup>

$\text{CF}_3\text{SOCH}_2\text{CF}_3$ , b.  $49-50^\circ$ .<sup>1</sup>

$\text{CF}_3\text{SOEt}$ , b.  $40-41^\circ$ .<sup>1</sup>  
 $(\text{CF}_3)_2\text{CFSOCH}_3$ , b.  $69-70^\circ$ .<sup>1</sup>  
 $\text{CF}_3\text{SOCH}_2\text{CH}_2\text{OSCF}_3$ , b.  $51-64^\circ$ .<sup>1</sup>  
 $\text{CF}_3\text{SOPr-i}$ , b.  $68-70^\circ$ .<sup>1</sup>  
 $(\text{CF}_3)_2\text{CFSOC}(\text{CF}_3)_2\text{F}$ , b.  $88-9^\circ$ .<sup>112</sup>

### Phosphorus

$\text{CF}_3\text{SPCl}_2$ , b.  $98^\circ$ .<sup>29</sup>  
 $(\text{CF}_3\text{S})_2\text{PCl}$ , b.  $115^\circ$ .<sup>29</sup>  
 $(\text{CF}_3\text{S})_2\text{PH}$ , b.<sub>149</sub>  $40^\circ$ .<sup>28</sup>  
 $(\text{CF}_3\text{S})_3\text{P}$ , b.<sub>30.5</sub>  $20^\circ$  (decomposes above  $50^\circ$ ).<sup>28</sup>

### Selenium

$\text{CF}_3\text{SSeNCO}$ , b.  $119^\circ$ ; m.  $-67^\circ$ ; Trouton's constant 20.8.<sup>25.5</sup>

### Silicon

$\text{CF}_3\text{SSiH}_3$ , b.  $13.6^\circ$ ; m.  $-127^\circ$ .<sup>21</sup>

## THIOL ACIDS

### Free Acids

$\text{CF}_3\text{COSH}$ , b.  $35.5^\circ$ ; n 27/D 1.3759.<sup>117</sup>  
 $\text{CHClFCOSH}$ , b.<sub>3</sub>  $43^\circ$ ; n 20/D 1.4320; d 20/4 1.470.<sup>33, 34</sup>  
 $\text{CHF}_2\text{COSH}$ , b.<sub>5</sub>  $70^\circ$ ; n 20/D 1.4880; d 20/4 1.688.<sup>34</sup>  
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{COSH}$ , b.  $80-2^\circ$ ; n 24/D 1.3470.<sup>117</sup>  
 $\text{H}(\text{CF}_2)_4\text{COSH}$ , b.  $124-6^\circ$ ; n 24/D 1.3470.<sup>117</sup>

### Esters

$\text{CF}_3\text{COSCF}_3$ , b.  $24-6^\circ$ .<sup>78</sup>  
 $\text{CH}_3\text{COSCF}_3$ , b.  $80-3^\circ$ ; n 25/D 1.3640.<sup>78</sup>  
 $\text{CBrF}_2\text{CClFCOSCH}_3$ , b.<sub>20</sub>  $74-5^\circ$ ; n 20/D 1.4570; d 20/4 1.810.<sup>135</sup>  
 $\text{CF}_2=\text{CFCOSCH}_3$ , b.<sub>230</sub>  $67-8^\circ$ ; n 20/D 1.4375; d 20/4 1.396.<sup>135</sup>  
 $\text{CF}_3\text{COSEt}$ , b.<sub>760</sub>  $90.5^\circ$ ; n 25.5/D 1.3755, n 0/D 1.3888; d 25.5/4 1.2338, d 0/4 1.2766.<sup>51</sup>  
 $\text{C}_2\text{H}_5\text{COSCF}_3$ , b.  $99-100^\circ$ ; n 25/D 1.3754.<sup>78</sup>  
 $\text{CH}_2\text{FCOSCH}_2\text{CH}_2\text{Cl}$ , b.<sub>33</sub>  $104-5^\circ$ .<sup>113</sup>  
 $\text{CH}_3\text{COSCH}_2\text{CH}_2\text{F}$ , b.<sub>20</sub>  $50-1^\circ$ ,<sup>55</sup> b.<sub>12</sub>  $41-2^\circ$ ,<sup>36</sup> b.<sub>100</sub>  $87^\circ$ ,<sup>25</sup> b.<sub>30</sub>  $58-9^\circ$ ,<sup>108</sup> n 25/D 1.4510,<sup>55</sup> 1.4525,<sup>25</sup> n 20/D 1.4525;<sup>108</sup> d 25/4 1.4041,<sup>25</sup> d 20/4 1.1451.<sup>108</sup>  
 $\text{CF}_3\text{CF}_2\text{COSEt}$ , b.<sub>760</sub>  $103^\circ$ ; n 24.1/D 1.3592, n 0/D 1.3707; d 24.1/4 1.3300, d 0/4 1.3765.<sup>51</sup>  
 $\text{CH}_2\text{FCH}_2\text{CH}_2\text{COSCH}_3$ , b.<sub>6</sub>  $54^\circ$ ; n 20/D 1.4587; d 20/4 1.1135.<sup>108</sup>

- $\text{CF}_3\text{CF}_2\text{CF}_2\text{COSEt}$ ,  $b_{760}$   $119^\circ$ ;  $n$  19.3/D 1.3544,  $n$  0/D 1.3631;  $d$  19.3/4 1.4217,  $d$  0/4 1.4618.<sup>51</sup>  
 $\text{CH}_3\text{COS}(\text{CH}_2)_4\text{F}$ ,  $b_{13}$   $76.5\text{--}78^\circ$ ;  $n$  25/D 1.4554.<sup>55</sup>  
 $\text{ClCO}(\text{CF}_2)_3\text{COSEt}$ ,  $b_{43}$   $101^\circ$ ;  $n$  25/D 1.4016.<sup>51</sup>  
 $\text{HO}_2\text{C}(\text{CF}_2)_3\text{COSEt}$ ,  $b_8$   $131^\circ$ ;  $n$  25/D 1.4070.<sup>51</sup>  
 $\text{CH}_2\text{FCOSPh}$ ,  $b_{18}$   $132^\circ$ ;  $m$ .  $36.5\text{--}37.5^\circ$ .<sup>113</sup>  
 $\text{CF}_3\text{COS}(\text{CH}_2)_5\text{SCOCF}_3$ ,  $b_8$   $119^\circ$ ;  $n$  24.8/D 1.4269,  $n$  0/D 1.4372;  $d$  24.8/4 1.3627,  $d$  0/4 1.3960.<sup>51</sup>  
 $\text{EtSCO}(\text{CF}_2)_3\text{COSEt}$ ,  $b_8$   $122^\circ$ ;  $n$  24.5/D 1.4351,  $n$  0/D 1.4446;  $d$  24.5/4 1.3858,  $d$  0/4 1.4178.<sup>51</sup>  
 $\text{C}_2\text{F}_5\text{COS}(\text{CH}_2)_5\text{SCOC}_2\text{F}_5$ ,  $b_8$   $128^\circ$ ;  $n$  23.8/D 1.4006,  $n$  0/D 1.4102;  $d$  23.8/4 1.4404;  $d$  0/4 1.4758.<sup>51</sup>  
 $\text{H}(\text{CF}_2)_4\text{COSC}_6\text{H}_{12}$ ,  $b$ .  $72\text{--}72.5^\circ$ ;  $n$  23/D 1.4085.<sup>117</sup>  
 $(\text{CF}_2\text{COSBu-}n)_2$ ,  $b_{70.01}$   $105^\circ$ ;  $n$  25/D 1.4719.<sup>107</sup>  
 $n\text{-C}_3\text{F}_7\text{COS}(\text{CH}_2)_5\text{SCOC}_3\text{F}_7$ ,  $b_8$   $142^\circ$ ;  $n$  24.5/D 1.3866,  $n$  0/D 1.3960;  $d$  24.5/4 1.5220,  $d$  0/4 1.5613.<sup>51</sup>  
 $(\text{CF}_2\text{COSC}_{10}\text{H}_7\text{-}2)_2$ ,  $m$ .  $130\text{--}131.5^\circ$ .<sup>107</sup>

#### Imido Esters

- $\text{C}_2\text{F}_5\text{C}(:\text{NH})\text{SCH}_3$ ,  $b_{78}$   $43.5^\circ$ ;  $n$  25/D 1.3811;  $d$  25/4 1.421.<sup>7</sup>  
 $\text{CF}_3\text{C}(\text{NH})\text{SEt}$ ,  $b_{56}$   $37.5\text{--}38^\circ$ ;  $n$  25/D 1.4072;  $d$  25/4 1.238.<sup>7</sup>  
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{C}(\text{NH})\text{SCH}_3$ ,  $b_{79}$   $55^\circ$ ;  $n$  25/D 1.3669;  $d$  25/4 1.496.<sup>7</sup>  
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{C}(\text{NH})\text{SEt}$ ,  $b_{27}$   $45^\circ$ ;  $n$  25/D 1.3713;  $d$  25/4 1.413.<sup>7</sup>  
 $\text{CH}_3\text{SC}(:\text{NH})(\text{CF}_2)_3\text{C}(:\text{NH})\text{SCH}_3$ ,  $m$ .  $125^\circ$  (dec.).<sup>7</sup>

#### Thiosulfate and Thiosulfonate Esters

- $\text{CF}_3\text{SO}_2\text{SCF}_3$ ,  $b$ .  $69\text{--}70^\circ$ ;  $n$  1/D 1.3480.<sup>46</sup>  
 $\text{HO}_2\text{SSC}(\text{CF}_3)_2\text{H}$ ,  $\text{NMe}_4$  salt,  $m$ .  $196\text{--}8^\circ$  (d);<sup>93</sup>  $\text{NEt}_4$  salt,  $m$ .  $165\text{--}6^\circ$ ;  $\text{NPr}_4$  salt,  $m$ .  $123\text{--}5^\circ$ .<sup>96</sup>  
 $\text{HO}_2\text{SSC}(\text{CF}_3)(\text{SCF}_3)\text{H}$ ,  $\text{NPr}_4$  salt,  $m$ .  $140\text{--}143^\circ$ .<sup>96</sup>  
 $\text{HO}_2\text{SSC}(\text{SCF}_3)_2\text{H}$ ,  $\text{NMe}_4$  salt,  $m$ .  $155^\circ$  (d).<sup>96</sup>  
 $2,5\text{-Cl}_2\text{C}_6\text{H}_3\text{SO}_2\text{SCCl}_2\text{F}$ ,  $m$ .  $90\text{--}3^\circ$ .<sup>73</sup>  
 $2\text{-CH}_3,5\text{-NO}_2\text{C}_6\text{H}_3\text{SO}_2\text{SCCl}_2\text{F}$ ,  $m$ .  $75\text{--}7^\circ$ .<sup>73</sup>  
 $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{SCCl}_2\text{F}$ ,  $b_{13}$   $182\text{--}6^\circ$ .<sup>73</sup>

### THIOCARBONYL COMPOUNDS

#### Thion Esters

- $\text{FCSOCH}_3$ ,  $b_{755}$   $66^\circ$ ;  $n$  17/D 1.4170;  $d$  17/4 1.1900.<sup>140</sup>  
 $\text{CF}_3\text{CSOCH}_3$ ,  $b$ .  $67^\circ$ ;  $n$  25/D 1.3711.<sup>95</sup>  
 $\text{CHClFCSOCH}_3$ ,  $b_{60}$   $59^\circ$   $n$  20/D 1.4726;  $d$  20/4 1.327.<sup>34</sup>

$\text{CHF}_2\text{CSOCH}_3$ , b.  $94^\circ$ ; n 20/D 1.4012; d 20/4 1.331.<sup>34</sup>  
 $\text{FCSOEt}$ ,  $b_{755}$   $84^\circ$ ; n 17/D 1.4200; d 17/4 1.1020.<sup>140</sup>  
 $\text{CHClFCSOEt}$ ,  $b_{60}$   $71^\circ$ ; n 20/D 1.4636; d 20/4 1.246.<sup>34</sup>  
 $\text{CHF}_2\text{CSOEt}$ , b.  $105^\circ$ ; n 20/D 1.3888; d 20/4 1.180.<sup>34</sup>  
 $\text{FCSOPr-}i$ ,  $b_{750}$   $78^\circ$ ; n 17/D 1.4110; d 17/4 0.9990.<sup>140</sup>  
 $\text{CF}_3\text{CHFCSOEt}$ , b.  $98-9^\circ$ ; n 20/D 1.3920; d 20/4 1.3167.<sup>34</sup>  
 $\text{CHClFCSOBu-}n$ ,  $b_{23}$   $81-3^\circ$ ; n 20/D 1.4572; d 20/4 1.162.<sup>34</sup>  
 $\text{FCSOPh}$ ,  $b_{40}$   $87^\circ$ ; n 19/D 1.5260; d 19/4 1.2048.<sup>140</sup>  
 $\text{CHClFCSOCylcohexyl}$ ,  $b_5$   $86^\circ$ ; n 20/D 1.4564; d 20/4 1.064.<sup>34</sup>

### Thion Anhydrides

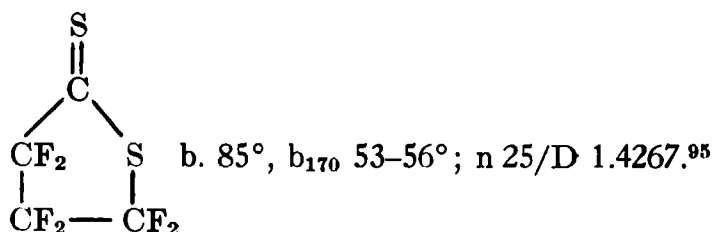
$\text{CHClFCSOAc}$ ,  $b_2$   $60^\circ$ ; n 20/D 1.3935; d 20/4 1.351.<sup>34</sup>  
 $\text{CHF}_2\text{CSOAc}$ ,  $b_4$   $55^\circ$ ; n 20/D 1.3869; d 20/4 1.358.<sup>34</sup>

### Thioacyl Halides

$\text{FCSF}$ , b.  $-57$  to  $-54^\circ$ ,<sup>93, 140</sup>  $-62.1 \pm 0.5^\circ$ ; m.  $-163.5 \pm 1^\circ$ .<sup>20</sup>  
 $\text{FCSCl}$ , b.  $9^\circ$ .<sup>92, 140</sup>  
 $\text{CBrF}_2\text{CSF}$ , b.  $41-2^\circ$ .<sup>95</sup>  
 $\text{CF}_3\text{CSCl}$ , b.  $28-9^\circ$ .<sup>95</sup>  
 $\text{CClF}_2\text{CSF}$ , b.  $22-23^\circ$ ,<sup>95</sup>  $18-20^\circ$ ,<sup>80</sup>  $36^\circ$ ;  $^{136}$  d 0/4 1.5183.<sup>136</sup>  
 $\text{CClF}_2\text{CSCl}$ ,  $b_{20}$   $-10^\circ$ ; n 25/D 1.4465.<sup>95</sup>  
 $\text{NCCSF}$ ,  $b_{123}$   $-1^\circ$  (in mixture with  $\text{CS}_2$ ).<sup>104</sup>  
 $\text{CF}_3\text{CSF}$ , b.  $-24^\circ$ ,<sup>80</sup>  $-21^\circ$ .<sup>93, 95</sup>  
 $\text{CHClFCSF}$ , b.  $56-7^\circ$ ; n 25/D 1.4182.<sup>43</sup>  
 $\text{CHF}_2\text{CSF}$ , b.  $14-16^\circ$ .<sup>43</sup>  
 $\text{CF}_3\text{CF}_2\text{CSF}$ , b.  $9^\circ$ .<sup>95</sup>  
 $\text{CH}_3\text{OCHFCSF}$ ,  $b_{0.9}$   $-13$  to  $-11^\circ$ .<sup>43</sup>  
 $\text{CF}_2=\text{CFCF}_2\text{CSF}$ , b.  $45-6^\circ$ .<sup>95</sup>

### Dithio Esters

$\text{FCS}_2\text{CF}_3$ ,  $b_{762}$   $42.9^\circ$ ,<sup>47</sup> b.  $42^\circ$ ;  $^{77}$  n 25/D 1.4010.<sup>77</sup>  
 $\text{FCS}_2\text{CH}_3$ ,  $b_{240}$   $78^\circ$ ; n 18/D 1.5645; d 18/4 1.200.<sup>140</sup>  
 $\text{CF}_3\text{CS}_2\text{CF}_3$ ,  $b_{50}$   $0^\circ$ ,  $\lambda$  cyclohexane/max 532 m $\mu$ .<sup>95</sup>  
 $\text{CF}_3\text{SCS}_2\text{CF}_3$ , b.  $110^\circ$ ,<sup>47</sup>  $b_{78}$   $61-3^\circ$ .<sup>77</sup>  
 $\text{FCS}_2\text{Et}$ ,  $b_{93}$   $73^\circ$ ; n 15/D 1.5041; d 15/4 1.1736.<sup>140</sup>



$\text{C}_2\text{F}_5\text{CS}_2\text{CH}_3$ ,  $b_{50}$   $51-2^\circ$ ;  $n_{25/D}$  1.4435;  $d_{25/4}$  1.455.<sup>7</sup>  
 $\text{CClF}_2\text{CS}_2\text{Et}$ ,  $b_5$   $51-2^\circ$ .<sup>95</sup>  
 $\text{CF}_3\text{CS}_2\text{Et}$ ,  $b_{54}$   $62^\circ$ ,<sup>7</sup>  $b.$   $134^\circ$ ; <sup>95</sup>  $n_{25/D}$  1.4593,<sup>7</sup> 1.4798; <sup>95</sup>  $d_{25/4}$  1.301.<sup>7</sup>  
 $\text{CHClFCS}_2\text{Et}$ ,  $b_{40}$   $60^\circ$ ;  $n_{20/D}$  1.4885;  $d_{20/4}$  1.330.<sup>34</sup>  
 $\text{CHF}_2\text{CS}_2\text{Et}$ ,  $b_{60}$   $80^\circ$ ;  $n_{20/D}$  1.4990;  $d_{20/4}$  1.261.<sup>34</sup>  
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{CS}_2\text{CH}_3$ ,  $b_{46}$   $62-3^\circ$ ;  $n_{25/D}$  1.4200;  $d_{25/4}$  1.530.<sup>7</sup>  
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{CS}_2\text{Et}$ ,  $b_{37}$   $71-2^\circ$ ;  $n_{25/D}$  1.4225;  $d_{25/4}$  1.459.<sup>7</sup>  
 $\text{CClF}_2\text{CS}_2\text{Ph}$ ,  $b_{1.5}$   $85-6^\circ$ ;  $n_{25/D}$  1.5876.<sup>95</sup>  
 $\text{CF}_3\text{CF}_2\text{CH}(\text{CH}_3)\text{OCS}_2\text{CH}_3$ ,  $b_6$   $41^\circ$ ;  $n_{20/D}$  1.4157;  $d_{20/4}$  1.387.<sup>82</sup>  
 $\text{EtOCS}_2\text{CH}_2\text{CH}_2\text{F}$ ,  $b.$  208–210.<sup>115</sup>

### Thio Amides

$\text{CF}_3\text{CSNH}_2$ ,  $b_2$   $40^\circ$ ; <sup>109</sup>  $m.$   $42-3^\circ$ .<sup>133</sup>  
 $\text{C}_2\text{F}_5\text{CSNH}_2$ ,  $b_{23}$   $60^\circ$ ;  $m.$  39–40.<sup>109</sup>  
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{CSNH}_2$ ,  $b_{21}$   $69^\circ$ ;  $m.$   $47-8^\circ$ .<sup>109</sup>  
 $(\text{CF}_3)_2\text{C}(\text{OH})\text{CSNH}_2$ ,  $b_{0.9}$   $70-76^\circ$ ;  $m.$   $52^\circ$ .<sup>17</sup>  
 $\text{FCSNet}_2$ ,  $b_{21}$   $100^\circ$ ;  $n_{15/D}$  1.4790;  $d_{15/4}$  1.0580.<sup>140</sup>  
 $\text{CHF}_2\text{CSNet}_2$ ,  $b_7$   $93^\circ$ ;  $n_{20/D}$  1.5220;  $d_{20/4}$  1.199.<sup>34</sup>  
 $\text{CF}_3\text{CHFCSNet}_2$ ,  $b_{10}$   $75-6^\circ$ ;  $n_{20/D}$  1.4662;  $d_{20/4}$  1.2758.<sup>35</sup>

### Thio Ketones

$\text{CF}_3\text{CSCF}_3$ ,  $b.$   $6^\circ$ ,<sup>79</sup>  $8^\circ$ ; <sup>54, 93, 95</sup>  $\lambda$   $\text{CH}_2\text{Cl}_2/\text{max}$  580  $\text{m}\mu$ .<sup>93, 95</sup>  
 $\text{CHF}_2\text{CSCF}_3$ ,  $b.$   $15^\circ$ ;  $d_{20/4}$  1.4463.<sup>35</sup>  
 $\text{CClF}_2\text{CF}_2\text{CSCF}_3$ ,  $b_{18}$   $-19^\circ$ .<sup>54, 95</sup>  
 $\text{CF}_3\text{CF}_2\text{CSCF}_3$ ,  $b_{200}$   $0^\circ$ .<sup>95</sup>  
 $\text{CHF}_2\text{CF}_2\text{CSCF}_3$ ,  $b_{20}$   $-27^\circ$ .<sup>54, 95</sup>

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# Thioelastomers

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### Introduction

This designation, thioelastomers, has been applied to a class of more or less rubber-like polymers characterized by having the chains interrupted by sulfur atoms, or groups of such atoms. The group of these which has attained to commercial importance is manufactured and sold under the name "Thiokol" (trademarked name of the products of the Thiokol Chemical Corporation). The discussion here will be based on the "Thiokol" group because it is typical of thioelastomers in general and its chemistry has been explored extensively.

The name "Thiokol" was given by J. C. Patrick to the polymeric ethylene polysulfide that results when ethylene chloride reacts with sodium tetrasulfide. "Thiokol" is from two Greek words meaning *sulfur* and *gum*. Of all the jointed polymers it is the one that is both simple to put together and easy to take apart. Its study has added much to our understanding of polymers. "Thiokol A," as this polymer is now known, was the first of a class, interesting scientifically as well as commercially. The development of the polysulfide polymers has run parallel to that of the polyesters and polyamides. The first "Thiokol" patent was the British patent 302,270, dated December 13, 1927, and noted in *Chemical Abstracts* for September 10, 1929.<sup>214a</sup> W. H. Carothers' first article on condensation polymers appeared in



the *Journal of the American Chemical Society* in August 1929, and in *Chemical Abstracts* for September 20th of that year. The chemistry and early applications of the polysulfide polymers, which were worked out by Patrick, almost singlehanded, have been developed by the Thiokol Corporation.

### JOINTED POLYMERS

Polymers are of two classes, jointed and continuous. A number of short pieces of glass tubing can be fused together to make one long tube. Or a long tube can be constructed by putting together sections with taper joints. The one may be broken into many pieces but the breaks may come anywhere, and the fragments will bear no relation to the original pieces. The jointed tube can be taken apart and the original sections recovered.

The extreme example of the first type is the polymerization of tetrafluoroethylene,  $F_2C:CF_2$ . Disregarding end groups, the product is a continuous chain of many thousands of  $-CF_2-$  groups, a section of which would look like this:



The original two-carbon units have lost their identity completely. A break in the chain is as likely to occur between the carbons of one of the original units as between two from different units. In polyvinyl acetate there are side  $-OAc$  groups at regular intervals but the carbon chain is continuous.

In the jointed polymers the carbon chain is not continuous but it interrupted by other atoms, such as oxygen, nitrogen, or sulfur. The simplest is polyoxymethylene:



Monomeric formaldehyde polymerizes spontaneously and the polymer can be taken apart readily—so readily, in fact, it may be used instead of the monomer in preparing formaldehyde derivatives. Here the sections go together and come apart just like the taper-joint sections of glass tubing mentioned before.

Polymers of ethylene oxide, trademarked as "Carbowax," have a similar structure but do not come apart so readily:



In both of these cases, if the end groups are disregarded, the polymers have the same composition as their constituent units.

$$\text{—COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}\cdot\text{O}\cdot\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}\cdot\text{O—}$$
$$\text{—OCH}_2\text{CH}_2\text{O}\cdot\text{COCO}\cdot\text{OCH}_2\text{CH}_2\text{O}\cdot\text{COCO}\cdot\text{OCH}_2\text{CH}_2\text{O}\cdot\text{COCO—}$$
$$-\text{CONHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NHCOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$$
$$\text{—COC}_6\text{H}_4\text{COOCH}_2\text{CH}_2\text{OCOC}_6\text{H}_4\text{COOCH}_2\text{CH}_2\text{O—}$$
$$\text{—NHCHRCONHCHRCONHCHRCONHCHRCO—}$$

Sulfur, as well as oxygen, or nitrogen, may connect the sections of a jointed polymer. A dimercaptan,  $\text{HS}(\text{CH}_2)_n\text{SH}$ , and a dihalide,  $\text{Br}(\text{CH}_2)_m\text{Br}$ , react in the presence of an alkali to form rings and linear polymers<sup>173, 278</sup> as has been discussed in chapter 1. Such a polymer is made up of repeating units,  $-(\text{CH}_2)_n-\text{S}(\text{CH}_2)_m\text{S}-$ . The terminals will be mercaptan groups or halogens according to which of the reactants is in excess. These also are jointed polymers which can be broken at the joints, though not easily. Sodium sulfide and ethylene chloride give the same sort of polymer, of which the repeating unit is  $-\text{CH}_2\text{CH}_2\text{S}-$ .

Ethylene chloride reacts even more readily with sodium disulfide, trisulfide, or tetrasulfide. The repeating units are  $-\text{SCH}_2\text{CH}_2\text{S}-$ ,  $-\text{SCH}_2\text{CH}_2\text{S}_2-$ , and  $-\text{SCH}_2\text{CH}_2\text{S}_3-$ . The products are jointed polymers but they differ from the monosulfide polymer in that they are readily disjointed. The disulfide polymer can be reduced to ethylene mercaptan by chemical means<sup>81, 171, 211</sup> or by catalytic hydrogenation.<sup>156, 242</sup> On the other hand, it can be made to take up sulfur. The tetrasulfide polymer is one that has that average composition. Some of the joints may contain one, two, or three sulfur atoms and others, five, or possibly six. The sodium polysulfide from which the polymer is made is known to be a mixture of all the possible sulfides from mono- to penta-. The polymer usually has approximately the same "rank" as the sodium polysulfide used to prepare it. The tetrasulfide is rank 4.

Sulfur may be removed from a high-rank polymer by boiling it with aqueous sodium hydroxide, sulfide, or sulfite, all of which take up sulfur. This desulfurization stops short at the disulfide stage no matter which, or how much, of these reagents is used. This is known as "stripping." The sulfur that is thus removed is chemically bound as is shown by the fact that it cannot be dissolved out by acetone.<sup>111, 115, 120, 198a, 200c, 212b, 244, 271b</sup>

### "THIOKOL"

Back in 1842 Löwig and Weidmann<sup>162</sup> added "chlorätherin," to alcoholic solutions of potassium trisulfide and pentasulfide. Curiously enough, the two products were practically identical, containing 85.41 and 84.99% of sulfur, respectively—the one from the trisulfide having slightly more sulfur than the other. Polymeric ethylene pentasulfide,  $(\text{CH}_2\text{CH}_2\text{S}_5)_n$ , should have 86.46%. Their product was a plastic mass which awakened no interest. They were interested in its composition and in finding that "ätherin" forms a pentasulfide just as potassium does. At that time the atomic weight of sulfur was 16 and potassium pentasulfide was  $\text{KS}_5$ . Exactly what their product was will never be known because the composition of their "chlorätherin" is uncertain. The addition of chlorine to ethylene looks like a simple reaction but the product is apt to be highly impure. In an attempt to duplicate their experiments, using pure ethylene chloride, the

products obtained had 79.0 and 81.5% sulfur, respectively, corresponding to  $C_2H_4S_{3.3}$  and  $C_2H_4S_{3.9}$ .<sup>72</sup>

While experimenting with ethylene chloride for quite a different purpose, Patrick caused it to react with sodium polysulfide and obtained a product that looked enough like rubber to attract his attention. Much had to be done, however, to convert this into a useful product. To carry out the reaction in aqueous solution, stirring and the addition of a dispersing agent were necessary on account of the low solubility of the ethylene chloride.

When an attempt was made to go to pilot plant scale production, a most serious difficulty was encountered: the polymer separated out in one rubbery mass which had to be dug out of the reaction vessel. Overcoming this difficulty was the discovery which made the large scale manufacture of "Thiokol" feasible. It was found that when the reaction is conducted in the presence of precipitated magnesium hydroxide and a suitable dispersing agent, the polymer comes down as fine granules which settle out when the agitation is stopped.<sup>203</sup> The supernatant solution can be syphoned off, and slurry washed by adding water, agitating, settling, and drawing off. This cycle can be repeated as often as necessary to remove dissolved salts. The slurry, which is called "latex," can be pumped to an open tank where it is coagulated by the addition of acid. The latex can be dewatered without coagulation.<sup>83b</sup>

Patrick's second discovery—the one that made the polymer useful—was that it can be vulcanized. This is accomplished with the same agents and under the same conditions as the vulcanization of natural rubber, except that sulfur does not have to be added. The change in properties is much the same. A vulcanized "Thiokol" resembles vulcanized rubber in many respects. According to Patrick,<sup>199</sup> the polysulfide links confer rubber-like properties on the polymer as do the double bonds in natural rubber. Early patents<sup>175, 204, 214a, 215b</sup> claimed products from the reaction of chlorinated olefins, such as ethylene and propylene chlorides, with sodium polysulfide, without saying much about operating methods.

The manufacture of "Thiokol" was begun in Kansas City in 1929 but was moved to Yardville, New Jersey, in 1930; and to Trenton in 1938. It has been manufactured also in Germany

and Japan.<sup>199</sup> The first product put out was "Thiokol A" which was made from sodium tetrasulfide and ethylene chloride with a little propylene chloride added to give a somewhat softer product. Numerous other varieties have followed. These differ from one another in the dihalides, or mixture of dihalides, used, in the rank of the sodium polysulfide, and also in methods of processing. The molecular weight of "Thiokol A" runs to 100,000 or higher. Of late, liquid polymers of low molecular weight have become important.

Many articles have been published on the manufacture, properties, and applications of "Thiokol." 6, 7, 14, 28, 29, 41, 43, 45, 48, 50a, 135, 137, 152, 155, 163, 168b 170, 171, 185, 198b, 215a, 218, 223, 234, 247a, 247b 250, 264, 298 Special attention is called to articles by Patrick,<sup>198a</sup> and by Fettes and Jorczak.<sup>76, 130</sup> There are many others on synthetic rubbers and elastomers which mention "Thiokol" 16, 22, 26, 31, 32, 46, 78, 94, 95, 96, 97, 99, 101, 126, 144, 146, 154, 219, 224, 226, 229, 232, 233, 251, 252, 253, 255, 260, 261, 262, 276, 285, 294 as well as recent reviews.<sup>18.5, 75.5, 76.5, 289.5</sup>

A wide variety of polysulfide polymers can be obtained by using different starting materials and by modifying the operating conditions. Some of the polymers are elastomers and others are plastics.

From ethylene chloride it was logical to go on to other dihalogen compounds. For proper reactivity it is desirable that both of the halogens be primary. Dichloroethyl ether,  $O(CH_2CH_2Cl)_2$ , has been used extensively.<sup>17, 105, 109, 116, 209</sup> Higher chlorinated ethers of this type, such as  $ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$ ,<sup>209, 271c</sup> dichlorohydrins,<sup>70, 75, 108, 116, 121a, 122, 158, 210e</sup> formals,  $H_2C(OCH_2CH_2Cl)_2$ ,<sup>49, 105, 110, 119, 237</sup>  $H_2C(OCH_2CH(OH)CH_2Cl)_2$ ,<sup>110, 119, 210e, 237</sup> acetals,  $RCH(OCH_2CH_2Cl)_2$ ,<sup>119</sup> other acetals,<sup>65</sup> mercaptals,  $RCH(SCH_2CH_2Cl)$ ,<sup>105, 110, 210e</sup> dibasic acid esters of ethylene chlorohydrin,<sup>194, 296</sup> and glycol esters of chloroacetic acid<sup>106, 118, 194</sup> have been claimed as reactants with metal polysulfides. A satisfactory product can be made from mustard gas, either crude or refined,<sup>1, 67c, 131, 199</sup> or from this mixed with ethylene chloride. That from mustard gas alone would contain alternate monosulfide and polysulfide joints. To produce the proper softness the addition of some propylene chloride is desirable.<sup>199</sup> Various other dihalides have been recommended.<sup>107, 145, 149, 193, 200b, 269, 280, 290</sup> A nitroalkyl chloride,<sup>188</sup> epi-

chlorohydrin<sup>105, 108, 116</sup> or other halogenated epoxides,<sup>222, 249</sup> and sulfated glycol ethers<sup>114</sup> react in the same way as dihalides. A mixture of two or more dihalides may be used so as to have sections of more than one kind in the polymer chain.<sup>64, 210b</sup> The presence of ammonia or of an organic base is said to influence the reaction beneficially.<sup>104, 105, 108</sup> Allyl chloride is said to give an elastomer with sodium polysulfide.<sup>113, 124</sup> Halogenated wood tars have been suggested.<sup>98</sup> The dihalide may contain reactive groups such as hydroxyl, carboxyl,<sup>74a, 228</sup> or alkoxy groups.<sup>243</sup> Sulfur may be added to a sodium sulfide solution in the presence of the dihalide.<sup>283</sup>

There are numerous patents by Baer on products from formaldehyde, methylene chloride, -bromide, and -iodide, and ethylene chloride with sulfur compounds. Some of the products appear to be monosulfides and others polysulfides.<sup>8, 9, 10, 11, 12, 13, 57, 247b</sup> Others have made polymers from formaldehyde,<sup>69.5, 142.5, 153, 206, 256, 263, 281, 284.5</sup> furfural,<sup>207</sup> acetaldehyde, glyoxal, and other aldehydes.<sup>263</sup> An aldehyde functions as a dihalide,  $\text{RCHCl}_2$ .<sup>256</sup> Polymers have been made from benzal chloride mixed with the usual dihalides.<sup>117</sup> The polymers from sodium sulfide and dichloromethyl ether,<sup>225</sup> epichlorhydrin,<sup>27</sup> or 1,4-dibromobutene-2<sup>246</sup> are monosulfide polymers but may be mentioned here since they are said to be elastomers.

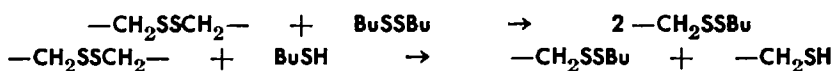
The reaction of ethylene chloride with metal polysulfides may be conducted in the presence of an alkylcellulose,<sup>136, 244</sup> an aldehyde,<sup>68, 167</sup> silicic acid,<sup>71</sup> vinyl polymers,<sup>179</sup> vinyl acetate,<sup>138</sup> or ligninsulfonate.<sup>221, 256</sup> Protective colloids and dispersing agents are used.<sup>187</sup> Sodium alginate has been recommended.<sup>132</sup>

A formal polymer, in reverse, can be made by causing formaldehyde to condense with dithiodiglycol,  $\text{HOCH}_2\text{CH}_2\text{SSCH}_2\text{CH}_2\text{OH}$ .<sup>210d</sup> Polymers may be obtained by oxidizing, or sulfurizing, dimercaptans such as  $\text{HSCH}_2\text{CH}_2\text{SH}$  or  $\text{HSCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SH}$ .<sup>167.5, 210a, 212a, 271a</sup> A dibasic acid ester of mercaptoethanol,  $\text{HSCH}_2\text{CH}_2\text{OH}$ , may serve as a dimercaptan.<sup>212d</sup> A wax-like polymer is obtained from a dithiol and a dibasic acid.<sup>212e</sup> Polymers can be made from the reaction products of dihalides with sodium thiosulfate.<sup>67, 279</sup> A dimercaptan and sulfur monochloride give a polymer.<sup>159</sup> An ether-disulfide polymer is formed by dehydrating dithiodiglycol by heating it with concentrated sulfuric acid.<sup>148, 192b</sup> It has been proposed to make polymers of

this type from the sodium derivative,  $\text{NaOCH}_2\text{CH}_2\text{SSCH}_2\text{-CH}_2\text{ONa}$ , and ethylene chloride.<sup>148</sup>

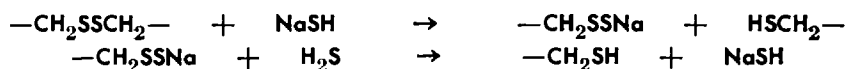
The reaction of a dihalide with a polysulfide should give a linear polymer of indefinite length. Polymers with molecular weights of several hundred thousands are commonly obtained. Cross-linking may be effected by mixing in a small proportion of a trihalide. The lengths of the chain may be limited by introducing a small amount of a monohalide as a chain-terminator.<sup>82, 83c, 199, 212c, 245a</sup> A compound of low molecular weight can be made by using a high proportion of the monohalide.

A polymer that has been precipitated as a "latex," while still in that form, can be modified in several ways. If the coagulation of a test sample gives a soft polymer of low molecular weight, the latex is heated with sodium polysulfide of high rank to toughen it by coupling up mercaptan terminals. The sulfur content, or rank, of the polymer may be raised by such treatment.<sup>83a</sup> On the other hand, the molecular weight may be reduced by heating with a mercaptan<sup>121b, 297</sup> or alkyl disulfide.<sup>121b</sup> If  $\text{-CH}_2\text{SSCH}_2\text{-}$  represents a section in the long polymeric chain, then:



Only a trifling amount of the low mercaptan, or disulfide, is required to cut the long chain into several pieces.<sup>19</sup> It is significant that a monosulfide polymer is not softened by this process.<sup>199</sup>

A disulfide link may be split by treatment with sodium hydrosulfide and hydrogen sulfide: <sup>77.5, 130, 212b</sup>



By regulating this treatment low polymers, with mercaptan terminals, of any desired average molecular weight may be obtained. Polysulfide polymers are convenient materials with which to study these reactions as the changes in molecular weights can be followed by viscosity measurements.<sup>19</sup> Currently, two liquid polymers, LP-2 and LP-3, with average molecular weights of 4000 and 1000, are manufactured. The manufacturing process has been described.<sup>264</sup> Formulae have been developed for calculating the amounts of reagents required for the preparation of

polysulfide polymers of any desired molecular weight and fluidity and having various terminal groups.<sup>74b</sup>

Several other ways of preparing polysulfide polymers have been proposed. A terpene dimercaptan is treated with a sulfur chloride.<sup>195</sup> Divinylacetylene and hydrogen polysulfide give a resinous product.<sup>37</sup> Heating a mixture of *p*-dichlorobenzene, 1,2,4-trichlorobenzene, sulfur, and sodium carbonate is said to give a resin.<sup>156.5, 156.6, 156.7, 156.8, 165, 166</sup> It has been proposed to use sodium polysulfide prepared in ethanol from sodium ethylate.<sup>192a</sup> Oxides or carbonates of magnesium, calcium, or barium may be substituted for the magnesium hydroxide.<sup>125</sup> A polymer has been made by treating a mixture of ethylene chloride, aniline, and formaldehyde with sodium polysulfide, or polyselenide, and then with phenol.<sup>90</sup> A disulfide polymer may be mentioned here, though it is quite different in structure. Polymeric *p*-mercaptostyrene is oxidised by iodine.<sup>196</sup>

Sodium polyselenides have been mentioned as alternates for sodium polysulfides.<sup>2, 90</sup>

The preparations of emulsions<sup>21, 64</sup> or suspensions<sup>245b</sup> of polysulfide polymers in water or in organic liquids has been described.

#### LABORATORY PREPARATION OF "THIOKOL TYPE A"

A convenient reaction vessel is a 5-liter flask with three necks into which are fitted a stirrer, a reflux condenser, and a dropping funnel. Two liters of 2-molar sodium tetrasulfide is placed in the flask. To this is added a solution of 8 g of sodium hydroxide followed by one of 20 g magnesium chloride ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ). This provides a precipitate of magnesium hydroxide. A wetting agent should be present; 1 g of "Nekal BX" is sufficient. The solution is heated to about 60°, the stirrer is started, and 3.8 moles of ethylene chloride is added dropwise from the funnel. As the reaction is exothermic the temperature rises. The ethylene chloride is added at such a rate that the temperature does not go much above 70°. Towards the end it may be necessary to supply some heat. On the plant scale, cooling is required. When the reaction is finished, the stirrer is stopped and the product settles as a granular powder—a sort of coarse latex. The mother liquor is siphoned off. The powder is washed by stirring it up with water and drawing off, repeating these operations as many



times as desired. The purified "latex" is poured into a beaker and coagulated by the addition of acid with stirring. This is the actual plant process in miniature and is used in the laboratory for trying out new dihalides and proposed variations in the process.<sup>199</sup>

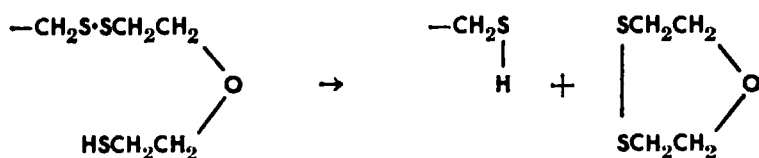
Directions for laboratory preparation have been given by others.<sup>19, 102, 127</sup>

#### ODOR AND DECOMPOSITION OF "THIOKOLS"

Some of the crude "Thiokols" have strong odors that may be attributed to the presence of monomeric dimercaptans or of volatile cyclic by-products. As is well known, cyclic monomers are formed along with linear polymers, the relative amounts of the two depending on spatial relationships, five- and six-membered rings being favored. Even sodium tetrasulfide contains enough of the monosulfide to permit the formation of cyclic monosulfides along with the linear polymers. An extreme case is the reaction of tetramethylene chloride with sodium tetrasulfide, in which tetramethylene monosulfide,  $(-\text{CH}_2\text{CH}_2)_2\text{S}$ , is formed to the exclusion of the linear polymer. Pentamethylene chloride, under similar conditions gives about 10% of pentamethylene sulfide and hexamethylene chloride only about 2%.<sup>73</sup> Steam distillation removes these volatile compounds and thereby improves the odor of the material. By using dihalides in which the terminal halogens are separated by a longer chain so that the formation of cyclic sulfides is not favored, odors can be eliminated almost entirely.

When some of the "Thiokols," in the latex form, are steam-distilled small amounts of oil collect in the condenser in pale yellow drops. The presence of alkali during the distillation accelerates the formation of these volatile oils. The amounts of these oils going over vary greatly with the type of "Thiokol." They are always small but may be as high as five to eight grams to a liter of distillate. The remarkable thing is that these oils continue to come over, day after day, at about the same rate as long as the steam passes through. On standing, these oils become opaque and are no longer volatile. They are then "Thiokol" polymers quite similar to the "Thiokols" from which they came. The sulfur content is of the same order, sometimes lower and sometimes higher but never lower than that of a disulfide.<sup>199</sup>

Steam-distillation of the polymeric disulfide from dichloroethyl ether,  $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{S}_2-$ , gives an oil that is stable enough and sufficiently abundant to be collected and characterized.<sup>51</sup> It was found to be the cyclic monomer,  $\text{O}(\text{CH}_2\text{CH}_2\text{S})_2$ , which has the same composition as the polymer. It is known that interchange takes place between a disulfide and a mercaptan. The polymer may be supposed to have a mercaptan terminal. The reaction would be represented:



It may be assumed that there is an equilibrium in which a very small amount of the cyclic monomer is present. As this is removed, more will be formed. It is to be noted that the polymer is left with a mercaptan terminal, so that the reaction may go on indefinitely. The polymer that remains is not sensibly altered. Clipping off a few units from the end of a chain of several thousand would not be expected to have much effect on its properties.

Similar phenomena are observed when "Thiokols" are heated to  $140^\circ$ . Vapors are given off which condense on a cold surface and turn to polymers. In one experiment with "Thiokol A" the rate was approximately the same for 120 hours. The rate is not proportional to the weight of the sample; for example, the condensate from 100 g heated for 40 hours was 1.4 g, compared with 1.0 g from 20 grams. The area of the surface is probably the important factor. A sample of "Thiokol A," compounded with zinc oxide and vulcanized, gave off vapors at about the same rate.<sup>199</sup> In a recorded case, 1000 g of a "Thiokol," kept at  $130\text{--}40^\circ$  for four hours, gave off 0.26 g of an irritating gas which had narcotic effect.<sup>157</sup>

In the vulcanization of "Thiokols," which is commonly effected at  $140^\circ$ , the escape of vapors is prevented by pressure. Hence there is no appreciable decomposition. Acrid odors are evident during the blending of a "Thiokol" with rubber on the warm rolls of a mill.

Assuming the correctness of the representation of the reaction as written here, the formation of the monomer must depend on the effective approach of the mercaptan terminal to a polysulfide

link. It has been found that the evolution of these vapors from "Thiokols," on steam-distillation, is much less when the chains between the sulfurs are longer. As explained before, the proportion of cyclic compounds originally formed is much less with these. The tetrasulfides from pentamethylene chloride and from the formal,  $\text{ClCH}_2\text{CH}_2\text{OCH}_2\text{OCH}_2\text{CH}_2\text{Cl}$ , give off negligible amounts of volatile cyclic monomers. The continued formation of the monomer must depend on its volatility. The tetrasulfide from the 1,3-dichlorhydrin,  $\text{ClCH}_2\text{CMe}(\text{OH})\text{CH}_2\text{Cl}$ , gives off no vapor, but that from  $\text{ClCH}_2\text{CHMeCH}_2\text{Cl}$ , does.<sup>199, 210c</sup>

These cyclic monomers, if they could be produced cheaply and sufficiently stabilized, should be most useful materials because they would polymerize with only slight changes in energy or volume.<sup>274</sup>

It has been proposed to deodorize "Thiokols" by treatment with super-heated water.<sup>139</sup> This would probably take care of low mercaptans and cyclics originally present. Grinding with copper or silver is said to be beneficial. This treatment might tie up the lower mercaptans. Barium sulfate is said to take up the odoriferous material.<sup>23</sup>

### STRUCTURE OF "THIOKOLS"

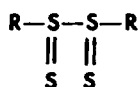
The first thing to consider is the structure of the long linear polymers that are obtained by the reaction of a dihalide with sodium polysulfide. "Thiokol A" may be taken as the simplest example. There can be no question as to the presence of the group  $-\text{SCH}_2\text{CH}_2\text{S}-$ . Stripping the tetrasulfide leaves polymeric ethylene disulfide, of which this must be the repeating unit, because further reduction gives the dimercaptan,  $\text{HSCH}_2\text{CH}_2\text{SH}$ .

Analogous statements can be made about the polymers that are made from other dihalides. The polymer from dichloroethyl ether must contain the unit  $-\text{SCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{S}-$ , which can be reduced to the dimercaptan,  $\text{HSCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SH}$ .

The open question is where the extra sulfurs are to be placed. Are they to be inserted between the disulfide sulfurs,  $-\text{CH}_2\text{S}-\text{SCH}_2-$ ; or are they to be attached in some way to these sulfur atoms?<sup>198a</sup> What are the structures of the  $-\text{S}_3-$ ,  $-\text{S}_4-$ , and  $-\text{S}_5-$  groups? One must look to Volume III, chapter 3 where monomeric polysulfides are considered and to chapter 5 Volume II, in which the by-products of mustard gas manufacture were

taken up.<sup>85</sup> A sharp distinction must be made between the fixed carbon to carbon and carbon to sulfur bonds and the labile sulfur to sulfur bonds.

The arrangement of the sulfur atoms in polysulfides has been investigated by both chemical and physical methods. The ready removal of two of the sulfurs from a tetrasulfide by sodium sulfide or sulfite led originally to the postulating of two sulfurs in the chain with two linked on the side (I), as opposed to a linear arrangement (II).



I



II

Early evidence by x-ray was interpreted to support structure I<sup>142, 270, 277</sup> or even a cyclic configuration of the sulfur.<sup>74</sup> The structure of polysulfides from the sulfur-olefin reactions,<sup>289</sup> and, in particular, the vulcanization of rubber,<sup>25, 72</sup> have been studied. *Bis*(chloroethyl)trisulfide and *bis*(iodoethyl)trisulfides have been shown to be linear by chemical evidence and x-rays,<sup>3, 52, 53, 85</sup> as is also dimethyl trisulfide.<sup>56</sup> Ultraviolet spectra of organic polysulfides also support the linear structure.<sup>13.5, 151, 235.5</sup> The chemists at Thiokol Chemical Company have come to accept the linear sulfur.<sup>18.5</sup> The evidence for linear configuration of sulfur has been discussed.<sup>235.6</sup>

In the discussion of the structure of polysulfides in Volume III (pages 89-91) it was pointed out that, although linkages between carbon and sulfur atoms are stable, those between sulfur atoms are labile. In view of this, there is little point to the discussion of the structure of groups of sulfur atoms. Alkyl tri- and tetrasulfides are statistical compounds; that is, they are mixture of higher and lower sulfides which have the percentages of sulfur corresponding to the formulas given.

"Thiokols" differ greatly in length of chain, or degree of polymerization. "Thiokol A" is a high polymer. The nature of its terminals is unknown. Analysis shows that only a minor proportion of them, if any, can be chlorine. Mercaptan groups seem to be absent. Hydroxyl terminals, from partial hydrolysis of the dihalides, may be present.<sup>77</sup> Before it is compounded and vulcanized, this polymer has to be plasticized on the mill by the

addition of small amounts of the required chemicals. The low polymers, which have mercaptan terminals, have to be cured by oxidation to disulfides. Zinc oxide plays an important, but little understood part.

### Vulcanization

After more than a hundred years of practice, the theory of the vulcanization of rubber is finally taking shape. According to Flory<sup>79</sup> the long polymeric molecules of raw rubber are entangled in a completely haphazard manner. In vulcanization these are cross-linked so as to form a network. The links that bind the chains together are pairs, or groups, of sulfur atoms. A piece of vulcanized rubber, whether it be a tiny bit or an automobile tire, may be considered a single mammoth molecule resembling a fish net in structure, except that it is in three dimensions instead of two and that the knots are irregularly distributed and relatively far apart. The effect of sulfur in linking unsaturated hydrocarbon chains is taken up in the next chapter, under *Factice*.

Curiously enough "Thiokols" are vulcanized under the same general conditions as natural rubber.<sup>58, 59, 77, 112, 201</sup> This discovery was a most important step in the development of "Thiokol."<sup>176</sup> The same accelerators and the same compounding ingredients, such as zinc oxide and carbon black, are used in the same ranges of temperature. The physical changes effected by vulcanization are remarkably similar in both cases. Nondescript semi-plastic masses are converted into highly elastic materials that can be stretched to many times their length and snap back when released. The stress-strain curves are similar. These and other properties depend on the particular formulations and curing conditions as they do with natural rubber. Elongations may run from 300 to 600%, and tensile strength from 1000 to 6000 psi, compared with 900% and 5000 lb for natural rubber. According to an early observation, stretched rubber and stretched "Thiokol" show the same X-ray pattern<sup>142</sup> but a later author found them quite different.<sup>239</sup> Published X-ray data on stretched polyethylene di- and tetrasulfides have been compared with those of other compounds.<sup>103</sup>

As the regular "Thiokols" already have high percentages of sulfur, no more has to be added. Actually, polymers that have been made so as to contain only disulfide linkages cannot be

vulcanized without the addition of sulfur. High sulfide polymers may be mixed with rubber to supply the sulfur necessary for vulcanization.

The changes effected in the vulcanization of "Thiokols" and of rubber are so strikingly alike that one can hardly escape the conclusion that the mechanisms of the two processes are at least partially similar. The crude "Thiokol" must consist of a mass of independent polymer chains all tangled together. In vulcanization, these may be supposed to become tied together at irregular intervals. This bonding may be through groups of sulfur atoms as in natural rubber.<sup>72</sup>

In the case of rubber, these cross-links have to be established by the reaction of sulfur with the hydrocarbon chains, the attack being on the methylene groups activated by the adjacent double bonds. In the "Thiokol" chains there are no activating double bonds, but there may be some other source of activation. The chlorination of mustard gas,  $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$ , takes place with extreme ease and the product is  $\text{ClCH}_2\text{CHClSCH}_2\text{CH}_2\text{Cl}$ , which indicates activation of the  $-\text{CH}_2-$  group by the adjacent sulfur atom. The sulfur necessary for the cross-linking may come from trisulfide or tetrasulfide linkages in the chain.<sup>198.5</sup> For a network similar to that of rubber, only one cross-linking sulfur group would be required for a hundred units. Multiplication of the cross-linking groups would result in a product similar to the hard solid, ebonite. In the manufacture of "Thiokols" some cross-linking is usually provided by mixing a small amount of a trifunctional halide such as 1,2,3-trichloropropane, with the difunctional halide.

Instead of establishing cross-links between long threads, a network may be constructed by splicing together the ends of short chains, some of which are branched. At the present time liquid polymers comprise a large proportion of the "Thiokols" manufactured. A typical example is LP-2, in the making of which a mixture of 98 parts of the formal,  $\text{ClCH}_2\text{CH}_2\text{OCH}_2\text{OCH}_2\text{CH}_2\text{Cl}$ , and 1,2,3-trichloropropane is used.<sup>130</sup> The average molecular weight is around 4000, which means that each chain contains about 24 links and that one chain in two is branched. These low polymers have mercaptan terminals. Oxidising these to disulfides should give a network. The formation of a mercaptide of a bivalent metal, and such as zinc, should have the same effect.

These low polymers are soluble in certain solvents.<sup>76</sup> A porous material such as leather can be impregnated with such solution and the solvent evaporated.<sup>49, 189</sup> The formation of a cross-linked, rubbery polymer of high molecular weight then takes place *in situ*. The curing agents are oxidising agents<sup>130</sup> but others have been suggested.<sup>161, 180</sup>

The similarity of a vulcanized "Thiokol" to rubber has been emphasized. Under quick compression or stretching the behavior is similar. The sudden stretching of a strip of a "Thiokol" develops heat as is the case with rubber. The stress-strain curves for "Thiokols" are similar to those of rubbers. There is, however, a difference between rubber and thioelastomers in the completeness of the recovery of shape of a test piece, after having been subjected to a heavy stress for a long time. The piece of thioelastomer is more or less deformed, the amount of the deformation depending on the magnitude of the stress, the time it has been applied, and particularly on the type of the polymer. This is known as *cold-flow*, or relaxation. There are wide differences among thioelastomers in the rate at which it takes place. The relaxation of "Thiokols" has been studied extensively by Tobolsky and associates.<sup>24, 91, 177, 254, 273, 275</sup> A major objective of research on "Thiokol" has been the elimination of cold-flow. It has been minimized in the commercial varieties to the extent that it does not interfere in many applications. Cross-linking by means of trifunctional halides helps.<sup>271d</sup> Some structural units give much better results than others.<sup>18, 267</sup>

The moldability of rubber may be supposed to be due to the interchange of sulfur bonds among the sulfur knots that tie the hydrocarbon chains into a network. In rubber, which may contain less than 1% of sulfur, these knots are sparsely distributed along the chains and have little opportunity of coming in contact with each other except at high temperatures where the mobility is greater. In the "Thiokols" there is such an abundance of polysulfide links that it is easy for one of them to come into contact with another. In fact, it is difficult to see how these bulky sulfur knots can escape close contact when the mass is put under stress. Changing the shape of a piece of a thioelastomer by stress does not alter its properties. Only the sulfur-to-sulfur bonds are involved and for every one of these that is broken one of exactly the same kind is established.

### Properties of Thiokols

In this section, "Thiokols" are treated as a class though there are large differences in the properties of various members of the group. Properties of the FA type have been more specifically described.<sup>128</sup>

The permeability to gases is low.<sup>5, 230</sup> To hydrogen and helium, the permeability of one variety is 6% of that of rubber, and of another "Thiokol," only 3%.

The "Thiokols" have outstanding resistance to hydrocarbon solvents. They are almost entirely indifferent to aliphatic hydrocarbons, but they swell slightly in aromatics.<sup>30, 36, 38, 42, 54, 86, 87, 89, 140, 141, 181, 183, 190, 191, 220, 231</sup> In this they are far superior to natural rubber. "Thiokols," however, differ among themselves in this respect, also. Solutions of certain of them in indene<sup>268</sup> and in sulfurized organic bases have been proposed.<sup>55</sup> The permeability of films of polysulfide rubber latex by water is reduced by exposure to aromatic vapors.<sup>259</sup>

The "Thiokols" are remarkably resistant to light, oxygen, and even ozone.<sup>168a, 171, 174, 177, 186, 288</sup> They are far superior to rubber in this respect. "Thiokol" 75% with 25% "Hycar-OR" is resistant to sunlight.<sup>88</sup>

The electrical resistance, dielectric constant, power factor, and breakdown voltage of a "Thiokol" have been compared with those of rubber and of several other elastomers.<sup>44, 133, 291</sup>

Different varieties of "Thiokols" differ considerably in density. "Thiokol A" which has the highest sulfur content—about 83%—has the highest density, 1.598. The density of some others is only a little above 1.<sup>295</sup>

The properties of the various "Thiokols" at low temperature vary with the composition and compounding. Some are elastic at quite low temperatures.<sup>40, 160, 178, 182, 184, 240, 241</sup>

The use of "Thiokol" in blends with rubber has made its detection and estimation important.<sup>150, 197, 284</sup> A color reaction has been devised.<sup>235</sup>

### Applications

"Thiokols" have been recommended for a wide variety of uses<sup>39, 196.5</sup> only some of which will be touched on here. Many of these have changed with time and new varieties of "Thiokols"



have been developed to suit. The first important use was for floater tops for gasoline tanks.<sup>35, 200a</sup> Its high resistance to hydrocarbons made it a "natural" for this. The gasoline tanks of fighter planes were made of rubber and lined with a "Thiokol." If a bullet penetrated one of these, gasoline going through the hole in the "Thiokol" would swell the rubber and stop the leak. "Thiokol" has been used for coating interiors of storage tanks for gasoline.<sup>50b, 227, 265</sup> Much "Thiokol" went into gasoline hose for filling stations and into the large hose used for filling tankers. This use declined with the development of synthetic rubbers, some varieties of which serve this purpose well enough.

At the beginning of World War II, when the supply of natural rubber was suddenly cut off, "Thiokol" attracted much attention. The materials for making it were at hand and the manufacture of it required only the simplest equipment. A special "Thiokol Type N" was developed for tires. Several firms, besides the Thiokol Corporation, took up the manufacturing and considerable amounts of it were made. Some tires were made from it and it served well for retreads. This development was cut short by the success of the National Scrap Drive, and Type N has not been manufactured since. The amazingly rapid development of synthetic rubbers pushed the "Thiokols" out of this and several other big markets, but they have found many smaller outlets, for which their special properties adapted them.

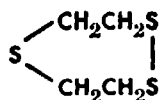
"Thiokols" and other polysulfide polymers have been recommended for electric insulation,<sup>134</sup> for coatings<sup>80, 123, 185, 236, 268</sup> on cables,<sup>205, 266, 293</sup> metals,<sup>34, 92, 100, 172</sup> and rubber.<sup>208</sup> They can be used for impregnating<sup>185, 268</sup> leather<sup>49, 189</sup> and fabrics,<sup>69, 145</sup> as fungicides<sup>256, 257</sup> and adhesives,<sup>66, 83c, 121c, 147, 185, 208, 286, 287</sup> for linings of acid pickling tanks, for floor coverings,<sup>208</sup> and for binders in paints<sup>217</sup> and chewing gums.<sup>164</sup> They can be prepared in films,<sup>4</sup> molded articles,<sup>208, 292</sup> and, when combined with other constituents, in flexible fabric sheets.<sup>93, 248</sup> Cork particles may be coated with a "Thiokol" and compressed.<sup>169</sup> A putty has been formulated from "Thiokol FA."<sup>128</sup> A polysulfide of low molecular weight with amyl terminals has been claimed as an additive for Diesel fuel.<sup>282</sup> An alkoxy-terminated low-polymer compound has been suggested for use in an extreme-pressure lubricant, and as an antioxidant.<sup>33</sup>

"Thiokols" may be blended with rubber,<sup>143, 202, 214b, 238</sup> with

phenol-formaldehyde resins<sup>63, 67b, 213</sup> or with other materials.<sup>20, 47, 93, 170, 248, 258, 272</sup> Polysulfide resins combine chemically with epoxide resins.<sup>75, 6, 123, 129, 187.5, 279.5</sup>

An interesting use of "Thiokol A" is in sulfur cements. As is well known, sulfur may assume the plastic state but soon becomes crystalline. The addition of 5% or less of "Thiokol A" to the sulfur keeps it in the plastic state indefinitely, thus enabling it to be used as a cement. The ethylene in such a mixture is less than one per cent.<sup>60, 61a, 62a</sup>

Sulfur plasticized with polysulfide polymers has been found useful in paints for marking roads.<sup>92.5</sup> Somewhat similar cements may be made by passing ethylene into sulfur at 120–60°. <sup>61b, 62b</sup> In experiments with sulfur and ethylene in solution in xylene a volatile sulfur compound accompanied the polymers. This appears to be ethylene sulfide-disulfide, or 1,2,5-trithiaheptane:



This is the sulfur analog of the 1,2-dithia-5-oxaheptane mentioned earlier.<sup>289</sup>

Heated to 205°, "Thiokol A" breaks down into a viscous oil which may be used as a plug-cock lubricant.<sup>216</sup>

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## CHAPTER 5

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# Factice

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The term *factice*—also written *factis*—from the French *caoutchouc factice*, meaning artificial rubber, has been applied to a variety of materials more or less resembling rubber. In the United States and Great Britain it is frequently called “Rubber Substitute.” \*

As the rubber has been dropped, from the name, the term *factice* might be applied to anything that is not a natural product, but it is commonly restricted to materials that have some of the elastic properties of rubber. This, however, is quite indefinite and no sharp line can be drawn to distinguish factices from a variety of other products such as plastics and resins.

The present day synthetic rubbers are more accurately *caoutchouc factice* or “Rubber Substitute” than any of the materials that are called factice, but they are excluded. Custom has narrowed the use of the name to products obtained by treating drying, or semi-drying, oils with sulfur or sulfur monochloride, and the designation *Vulcanized Oils* or *Vulcanized Vegetable Oil* has become more and more accepted. As there are such oils and as either treatment may vary, there are considerable differences in the products. Two varieties are distinguished, *dark factice*, made by heating oils with sulfur, and *white factice*, made by

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\* One manufacturer in the United States has copyrighted the name “Factice.”

mixing the oil with sulfur monochloride, avoiding high temperatures. Both products are solid, or semisolid, polymeric gels.

Somewhat similar materials may be obtained in various ways without the use of sulfur, such as by heating a drying oil in air or with an oxidising agent. Patents referring to such products are to be found listed in bibliographies on factice but they are not considered here.

As they are empirical mixtures rather than definite chemical compounds, factices may seem foreign to this book; however, the linking of a carbon atom to another carbon atom by sulfur takes place in their formation. Factices are, in part at least, sulfides, or polysulfides,  $\text{RSR}'$ , or  $\text{RS}_x\text{R}'$ , even though we do not know at just what points in the complex R and R', the ends of the sulfur bridges are located. The entrance of sulfur into the molecule is conditioned by the double bond and from the studies of the reactions of sulfur with simpler unsaturates, reasonable suppositions can be made as to what goes on with more complex molecules. As at least some of the sulfur links contain two or more sulfur atoms, factices belong with disulfides. The subject can be treated only briefly. Reference should be made to a number of papers.<sup>3, 40, 45b, 53, 57, 65, 82, 111, 151, 182, 189</sup>

### History

The bodying of linseed and other drying oils by heating in air has been practiced for a long time. It was natural for experimenters to try to improve this process by the addition of various materials. Sulfur must have been one of the more promising. Doubtless products of the factice class were obtained from time to time but, as there is no precise definition of a factice, it is impossible to say when the first factice was prepared and by whom. The Chinese appear to have pioneered in this line as in others.\*

Alexander Parkes describes the vulcanization of linseed, rapeseed and castor oils with sulfur chloride.<sup>125.5</sup> He is also credited with recognizing the similarity to the vulcanization of rubber. In this as in other cases it is difficult to trace the development of

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\* These statements apply to dark factice which was the only kind known until 1849 when Nickles and Rochelder discovered the reaction of sulfur chloride with drying oils.<sup>120</sup>

a product on account of the jealousy with which trade secrets were guarded by individuals and even by companies.

The history of factice has been sketched by Kirchhof,<sup>101</sup> Ruffel,<sup>147</sup> and Esch,<sup>60b</sup> and annotated patent lists have been given by Ditmar,<sup>46</sup> Halen,<sup>74</sup> Whalley,<sup>185</sup> Kirchhof,<sup>101</sup> Breuer,<sup>24</sup> and others.<sup>141</sup>

### Dark Factice

Dark factice is prepared by heating a drying oil, semi-drying oil, and other unsaturated fatty oils, such as castor or rapeseed oil, with sulfur. The oil is heated for some time at 100–130°, in a double-walled kettle with an agitator, to get rid of moisture. The sulfur is added with stirring and the temperature is raised to 150° or higher. The oil with dissolved sulfur begins to turn red-brown and foams slightly, evolving steam and hydrogen sulfide. The viscosity increases slowly. For rapeseed oil a minimum of 10% of sulfur is required, but 14 to 17% is commonly used. Next comes the period of polymerization in which the oil is heated for several hours at 157–160°. It becomes more and more viscous and finally a test portion solidifies on cooling. This process can be hastened by heating to 170° with the addition of a small amount of sulfur, or by the use of vulcanization accelerators. Some acrolein may be given off along with hydrogen sulfide. Finally the temperature is lowered to 120–130° and kept there for 24–28 hours.<sup>101</sup>

With rapeseed oil the iodine number changes only slightly on the addition of 14% of sulfur but it rises from 104 to 182 when 11% more sulfur is added.<sup>3</sup>

### CHEMISTRY OF FORMATION

The chemistry of formation of factice is still obscure. The sulfur is taken up but the amount of hydrogen sulfide evolved is comparatively small. There appear to be analogies between the formation of factice and the vulcanization of rubber,<sup>77</sup> though the amounts of sulfur involved are very different. The amount in factice is nearer the amount in the formation of ebonite. They are alike in that, for both, practice has preceded scientific understanding by a full century. Of the two, the reaction for factice is the more complicated, because different parts of a triglyceride molecule may react in different ways. Besides, any given

oil is a mixture of glycerides. Much can be learned from recent studies of the action of sulfur and sulfur compounds on olefins under vulcanizing conditions.<sup>22, 36.5, 119</sup> The difference of the sulfur molecule at different temperatures may be involved.<sup>101.5</sup>

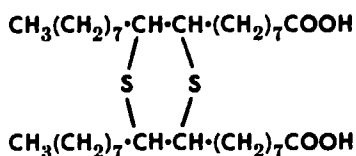
In one study of the factice reaction, triolein was used instead of a natural oil.<sup>167</sup> The factice from 250 g of triolein and 50 g of sulfur heated at 150–60° was separated into three portions by extraction, first with acetone, followed by petroleum ether. The portion taken out by acetone was a viscous oil with a molecular weight of about 1000. The addition of 20% of sulfur to triolein (molecular weight 884) would give 1051 if there were no loss. The next extract was more viscous and had a molecular weight around 2200. The residue was solid and insoluble in organic solvents, though it swelled in benzene. Curiously enough all three fractions showed practically the same sulfur content, 16.1–16.8 per cent. The sulfur calculated for simple addition is 16.57%. This figures out to be 5.4 atoms of sulfur for each triolein molecule.

Saponification of all three fractions gave acids which proved to be practically identical. The molecular weights were 807–891, showing them to be substantially trimers. The sulfur content, 13.4 to 13.9%, corresponds to 4.2 atoms of sulfur to each trimeric acid molecule. This shows a loss of 1.2 atoms of sulfur for each sulfurized triolein molecule. It was concluded that this part of the sulfur was in the glycerol portion, but a more reasonable supposition is that some of the chains had been joined by tri- or tetrasulfide linkages.

It has been shown in the chapter on "Thiokol" that extra sulfur atoms of a polysulfide link can be removed by alkali, leaving the disulfide link intact. In one case one third of the combined sulfur was removed from a vulcanized oil by treatment with lithium aluminum hydride.<sup>36.6</sup> Organic polysulfides can also be desulfurized to disulfides by the action of metallic oxides, amines, ammonia, and other reagents.<sup>114.5</sup> Experiments with films of these substances on water showed that the triolein and its sulfurized products, of both high and low molecular weights, form monomolecular layers of practically the same thickness, but the areas occupied by the sulfurized products are much larger.<sup>105</sup> The action of sulfur on linseed oil has been investigated.<sup>186</sup>

The problem has been approached in another way.<sup>16, 44, 97, 98</sup>

It is known that thiocyanogen can be added to unsaturates to form vicinal dithiocyanates and that these may lose thiocyanogen sulfide, leaving episulfides. Thus ethylene dithiocyanate gives ethylene sulfide. In the case of the thiocyanogen addition product with elaidic acid, this is supposed to take place intermolecularly so as to form a dithiane derivative:



Such acids are supposed to be involved in the formation of factice.<sup>148</sup> It is known that episulfides may be formed by the addition of sulfur to unsaturates.<sup>101</sup> Episulfides may rearrange into dithiane derivatives. This accounts for only one sulfur atom per molecule of the unsaturated acid.

Much light is thrown on the factice reaction by a recent study of the reaction of sulfur with several unsaturated hydrocarbons.<sup>62</sup> Cyclohexene is the simplest example. It was heated with sulfur at 140° and the products were separated by distillation in a high vacuum. There was no change in the carbon-hydrogen ratio, and no loss of hydrogen sulfide or mercaptan. The several products isolated could be represented by the formula  $\text{C}_6\text{H}_{11}\text{S}_x\text{C}_6\text{H}_9$ , in which one alkyl has more hydrogen and the other less than cyclohexene,  $\text{C}_6\text{H}_{10}$ . This was the average composition; there seemed to be some  $\text{C}_6\text{H}_{11}\text{S}_x\text{C}_6\text{H}_{11}$  and some  $\text{C}_6\text{H}_9\text{S}_x\text{C}_6\text{H}_9$  present. The fractions isolated were the monosulfide, disulfide, trisulfide, and tetrasulfide. There remained an undistillable residue of higher sulfides. The amount of monosulfide was relatively small. The authors suggest that the sulfur molecule,  $\text{S}_8$ , breaks into fragments,  $-\text{S}-$ ,  $-\text{S}\cdot\text{S}-$ ,  $-\text{S}\cdot\text{S}\cdot\text{S}-$ , and so on—and that these serve to join the two alkyls. It is to be remembered that the polysulfides are in equilibrium with one another and with sulfur.

One can imagine that sulfur attacks the methylene group adjacent to the double bond to give  $-\text{CH}:\text{CH}\cdot\text{CH}(\text{SH})-$  or  $-\text{CH}:\text{CH}\cdot\text{CH}(\text{S}_x\text{H})-$ . If these are added to cyclohexene, the products would be  $\text{C}_6\text{H}_9\text{SC}_6\text{H}_{11}$  and  $\text{C}_6\text{H}_9\text{S}_x\text{C}_6\text{H}_{11}$ . Going back to the triolein experiments, it appears that the sulfurization at 140° is mainly intramolecular, and that the oleic acid chains of a single glyceride molecule are bound together by links consist-



ing of one, two, or more sulfur atoms. The 4.2 atoms of sulfur per molecule, after saponification, would account for two  $\text{—S—}$  linkages to about one  $\text{—S—S—}$ . Before saponification there would have been  $\text{—S}_3\text{—}$  and  $\text{—S}_4\text{—}$ , etc., linkages. This is certainly an oversimplification, because many varied reactions go on in such a complicated system.<sup>136.5</sup> Alcoholysis of vulcanized triolein with amyl alcohol resulted in amyl esters of a dibasic acid which consisted of two oleic acids cross-linked by  $\text{—S—S—}$ , one acid retaining its original double bond.<sup>158.5</sup> This can be explained by assuming that the substitution of  $\text{—S—SH}$  for a methylene hydrogen and the addition of this across the double bond of the other molecule.

For a given oil, there is a minimum percentage of sulfur required to produce a factice. The addition of more sulfur causes progressive changes in properties but does not effect a radical alteration in the character of the product. If an excess of sulfur is used some will crystallize out. These facts are in accordance with the idea that increasing the sulfur simply raises the proportion of  $\text{—S}_3\text{—}$ ,  $\text{—S}_4\text{—}$ , etc., linkages relative to the  $\text{—S—}$  and  $\text{—S}_2\text{—}$ .

So far no way has been found to follow the reactions that take place in the second stage, when the sulfurized mixture is heated to  $160\text{--}180^\circ$ . The evidence given above indicates that, in the first stage, the triolein molecules are sulfurized intramolecularly with little interaction of the molecules. That is the triglyceride of the monobasic oleic acid has been converted into the triglyceride of a sulfurized trioleic acid, a tribasic acid. At the higher temperatures interchange of esters will take place, as in the formation of alkyd resins, rearranging the single triglycerides into a polymeric mass. Gelation occurs when the two-dimensional sulfurized triglyceride plates link together to form tri-dimensional structures.<sup>75.5</sup> The theoretical point of gelation has also been calculated, using Flory's equation for the formation of an infinite network in polymerization reactions.<sup>63.5</sup> Using 20 parts of sulfur on an "ideal" oil (MW 968, one double bond per fatty acid, which roughly corresponds to rapeseed oil), in the calculation it was assumed that gelation should occur when 87% of the unsaturated chains will have reacted with 61% of the added sulfur.<sup>67.5</sup> At higher temperatures, sulfur may be transferred from tetra- or pentasulfide links to lower sulfur links, or to the hydrocarbon

chains. Interchange between alkyl disulfides occurs at such temperatures:



It may be assumed that this goes on among the sulfurized acids.

If fatty oils of different composition, e.g., castor and soya bean, are vulcanized together, there appears to be cross-linking between the different oil molecules at even a low degree of vulcanization. Such co-vulcanized oils were shown to react differently from a mixture of the same oils vulcanized separately.<sup>131,3</sup>

In the consideration of factices, the presence of saturated acids in the glycerides is commonly ignored. A factice can be made from cottonseed oil, in which palmitic and stearic acids are abundant, the unsaturation being concentrated in the linoleic part. The palmityl and stearyl acids are probably present in mixed glycerides according to the assumed "even distribution" in natural fats.<sup>79,5</sup>

Esters of mono-, di-, and tri-unsaturated acids, heated to the same initial temperature with the same percentage of sulfur, showed rises in temperature roughly proportional to the degree of unsaturation. The darkening also increases with the unsaturation. For the tri- esters the time of gelation was also shorter.<sup>36,5</sup>

#### MAKING DARK FACTICE

As no limits have been set to variations either in starting materials or in processes for making factices, the field has been wide open for all and sundry. There are scores of patents, many of which are difficult to classify. No patents are mentioned here that do not include the use of sulfur, but it makes quite a difference whether 2% or 30% of sulfur is used, and whether the mixture is heated at a low or high temperature. Some patents claim the use of sulfur and/or sulfur chloride. Reference should be made to articles that describe the making of factices.<sup>1, 3, 17, 48, 73, 101</sup> The suitability of drying, semi-drying, and non-drying oils has been discussed,<sup>103</sup> and experiments have been conducted to establish differences in time and temperature of gelation, emission of hydrogen sulfide, effects on color, etc.<sup>36,5, 36,7</sup>

Various unsaturated oils have been heated with sulfur:<sup>93a</sup> corn oil,<sup>63</sup> linseed oil,<sup>18, 20, 34, 95, 158</sup> vegetable oils,<sup>42, 124, 158, 172</sup> fish oils,<sup>127, 169</sup> chrysalis oil,<sup>112,5</sup> and halogenated oils.<sup>23, 136</sup> Many

substances have been mixed with such oils before sulfurizing: mineral oils,<sup>109</sup> resins,<sup>4</sup> tar or bitumen,<sup>27</sup> stearin pitch,<sup>75,7, 134</sup> seaweed,<sup>30</sup> Johnson grass juice,<sup>75</sup> and rosin.<sup>102</sup> The sulfurizing process is said to be hastened by the addition of aromatic<sup>19</sup> or secondary aliphatic amines<sup>143</sup> or vulcanization accelerators.<sup>15</sup> The addition of sodium nitrite is said to be beneficial.<sup>90</sup> The pretreatment of the oil with certain inorganic salts has been recommended.<sup>8, 9, 10, 11, 50, 69</sup> An animal or vegetable oil is heated with hydrogen polysulfides or with sulfur and hydrogen sulfide.<sup>2, 70, 131</sup>

Factices have been made by sulfurizing turpentine,<sup>132, 133</sup> rosin and turpentine,<sup>29, 104</sup> rosin, pitch, asphalt, and wood oil,<sup>191</sup> isoprene,<sup>12</sup> polymerized vinyl acetate,<sup>37, 112</sup> or dimethylbutadiene,<sup>81</sup> acrylates,<sup>25</sup> vinyl chloride,<sup>139</sup> conjugated diolefins,<sup>168b</sup> low polymerized butadiene,<sup>101.5</sup> and depolymerized natural rubber. Esters of polybasic acids with ethylene glycol, compounded with sulfur, are said to give superior products.<sup>39</sup> Lubricating oils have been made by sulfurizing esters in which either the acid or the alcohol is unsaturated.<sup>159</sup>

An oil, such as rapeseed, may be sulfurized by heating it with an organic compound rich in labile sulfur such as "Thiokol A."<sup>13</sup>

Unsaturated hydrocarbons may be polymerized and then heated with sulfur.<sup>36, 89, 173</sup>

To produce harder, finer materials, clay,<sup>116, 170</sup> asbestos,<sup>80, 116</sup> and powdered slate<sup>140</sup> have been added to the oils before sulfurizing. Thixotropic colloids have been added to factices.<sup>100</sup>

### White Factice

#### CHEMISTRY OF FORMATION

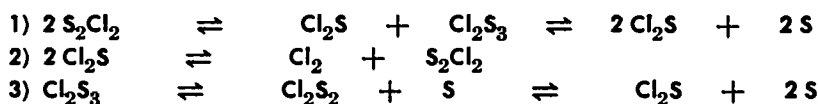
The chemistry of formation of white factice may be supposed to be analogous to the formation of mustard gas from ethylene and sulfur chloride, which has been satisfactorily worked out (see chapter 5, Volume II). Ethylene unites readily with sulfur dichloride to form chloroethane-sulfonyl chloride:



This, in turn, reacts with more ethylene:



The chlorides of sulfur are in highly mobile equilibrium with one another and with sulfur and chlorine:

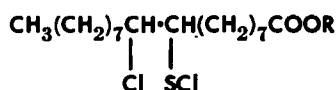


Ethylene reacts preferentially with chlorine monosulfide but also with the higher sulfides, particularly the trisulfide:

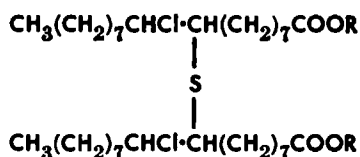


Actually the product may contain still higher sulfides, up to  $\text{ClCH}_2\text{CH}_2\text{S}_5\text{CH}_2\text{CH}_2\text{Cl}$ . These may be formed by sulfurizing the trisulfide or directly from chlorine polysulfides. Under some conditions a large proportion of the sulfur may separate as such. In such a case there is more of the monosulfide and less of the polysulfides.

The analogous reaction of sulfur dichloride with an oleic ester would give the sulfenyl chloride:



This would unite with a second molecule of the ester to form the monosulfide:

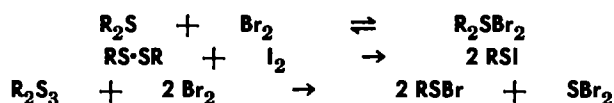


The chlorine trisulfide formed according to equation 1 may react so as to give  $\text{S}_3$  links between the chains; or may dissociate into the dichloride and sulfur, which will then be free to sulfurize in some other way. According to this scheme, the chlorine atoms are on carbons adjacent to those linked to sulfur which would make them very reactive. They might attack hydrogen of methylene groups adjacent to double bonds. In accordance with the structure shown, saponification removes all of the chlorine but none of the sulfur. The analogy to mustard gas might suggest vesicant action, but the much simpler compound,



is practically devoid of such properties.<sup>180</sup> A variety of reactions may go on in such a complicated system.

In a factice formed according to this mechanism the long acid chains would be linked together by  $-\text{S}-$ ,  $-\text{S}\cdot\text{S}-$ ,  $-\text{S}_3-$ , etc. In this respect, white factice should resemble the dark product. Actually the two classes have much in common. In the making of dark factice, sulfurizing should diminish the unsaturation by half, and the addition of sulfur chloride should eliminate it entirely. This cannot be tested by taking iodine numbers because halogens react with alkyl sulfides, disulfides, and polysulfides:



The investigations quoted give plausible explanations of what goes on in the factice reactions but much more work will have to be done before we can be certain. The action of sulfur monochloride on rubber has been supposed to tie the chains together with sulfur links.<sup>133.5, 184.5</sup>

#### MAKING WHITE FACTICE

The manufacture of white factice is comparatively simple. The oil, usually a vegetable oil such as rapeseed, is mixed with sulfur monochloride. The reaction is spontaneous and exothermic. Unless it is controlled, hydrogen chloride is evolved and an inferior product results. It is controlled by adding the sulfur chloride in portions and by cooling.<sup>3, 101</sup> Rapeseed oil reacts at  $-15^\circ$ .<sup>184.5</sup>

The amount of sulfur chloride taken up by an oil depends on its unsaturation; an oil may be said to have a *sulfur chloride number*. Theoretically this should be 26.6% of the iodine number. Rapeseed, with an iodine number from 104 to 130, takes up 25 per cent. The amount of sulfur chloride taken up by a film of an unsaturated oil is determined by exposing it to the vapor and noting the gain in weight. It is always less than the calculated figure.<sup>96</sup> To take care of traces of hydrogen chloride that may be set free, a small amount of a base, such as magnesia, is added. On cooling, the reaction product sets to a hard friable mass which is ground up for mixing with other materials.

Ditmar has reviewed the patent literature.<sup>46</sup> He and others have described the process of manufacture.<sup>45b, 45c, 45d, 155, 183</sup>

Colza,<sup>48</sup> cottonseed,<sup>48, 108</sup> castor,<sup>153</sup> and grapefruit seed<sup>110</sup> oils have been used. The addition of sulfur chloride raises the viscosity of cottonseed oil from 68 to 560 centipoises; that of olive oil, from 79 to 3422.<sup>144</sup> With olive oil, in which the unsaturation is due to a large proportion of oelic acid, the viscosity increases forty times, whereas with cottonseed oil, in which the unsaturation is greater but concentrated in a smaller proportion of linoleic acid, the viscosity increases only eight times. The use of water,<sup>21, 5</sup> ammonia,<sup>114, 176</sup> or an ammonium salt,<sup>67</sup> or an amine,<sup>176, 177</sup> along with the sulfur chloride has been recommended. Ultrasonic waves are said to speed up the formation of a factice.<sup>118</sup>

Several patents on ways of making white factice are listed.<sup>21, 135, 145, 156, 160, 161, 181</sup> High pressure has been recommended.<sup>137</sup> Butyric acid,<sup>146, 152</sup> rosin,<sup>64, 108, 146</sup> and petroleum<sup>64</sup> have been added to the oils. The oils that are to be used may be given pretreatments.<sup>94</sup> Instead of the usual oils, various materials have been claimed, such as tall oil residues,<sup>41</sup> pitch, wood oil,<sup>190</sup> divinylacetylene,<sup>28</sup> cuprene,<sup>58</sup> shellac,<sup>180</sup> polymerized isobutylene,<sup>86, 168a</sup> and phenolic resins.<sup>149a</sup> The gradual darkening of factice has been attributed to lipases in the oil.<sup>52, 54</sup>

It is claimed by some that it is better to heat the oil with a moderate amount of sulfur, cool it and add sulfur chloride to finish it off.<sup>68, 129, 165, 166, 175</sup>

A new method of preparing factice has been proposed. The oil, dissolved in carbon tetrachloride, is chlorinated in the presence of magnesium carbonate and the product is treated with aqueous sodium sulfide.<sup>64, 5</sup>

### Analysis and Estimation

Considerable attention has been given to the analysis<sup>5, 32a, 79, 113, 117, 179</sup> and testing of factices.<sup>32a, 113</sup> A white factice may have from 6.3 to 6.9% of sulfur and 5.0 to 7.6% of chlorine, and a dark factice, 3.2 to 12.7% of sulfur.<sup>179</sup> The free sulfur in white factice should be less than 0.5%, whereas in the dark product it may run from 1 to 8 per cent.<sup>66</sup> Testing apparatus has been described.<sup>45a</sup> Methods have been proposed for the complete analysis of both white and dark factices with specifications.<sup>71</sup> Attention has been given to the detection and estimation of factice in mixtures containing it.<sup>43, 79, 174</sup>

### **Applications**

Fully vulcanized oils are non-thermoplastic solids. There are numerous articles that discuss the use of factices,<sup>123, 182</sup> particularly with rubber.<sup>38, 40, 45b, 58, 65, 75.5, 83, 107, 128</sup> Its special characteristic is to improve plasticity and thereby the mold-flow and extrudability of uncured rubber or synthetic elastomer at elevated curing temperatures until the rubber itself becomes dimensionally stable by its own vulcanization. By itself or in rubber compounds, it also can absorb and retain several times its own weight of liquid plasticizers. It may be dispersed with rubber latex.<sup>125, 142, 164</sup> The effects on the vulcanization of the rubber have been studied.<sup>14, 47</sup> It has been mixed with rubber in cable insulation.<sup>55, 60a, 60b, 150</sup> It is an extender for rubber,<sup>126</sup> and up to 20% does not impair its properties.<sup>154</sup> One writer says up to 30%,<sup>45d</sup> but this is a broad statement. Much depends on the type and quality of the factice and on the purposes for which the rubber is intended.

Different factices impart different physical qualities to their blends with natural rubber, both during processing and in the finished product.<sup>63, 4</sup> The effects of different kinds of factice on the oil-resistance of Neoprene have been studied.<sup>32b</sup> White factice has been recommended as a corrosion-resisting coating.<sup>138</sup> Loaded with barium sulfate it serves as a screen to protect against X-rays.<sup>138</sup> Either white or dark factice is suitable for linoleum.<sup>99</sup> White factice from jojoba oil can go into linoleum<sup>59b</sup> or into printing ink.<sup>187</sup> Hot-vulcanized factice can be dispersed by the action of very small additions of amines for use in coatings, paints, etc.<sup>132.5</sup> Colors may be introduced into rubber by compounding it with a factice into which a colored material has been incorporated.<sup>85</sup>

### **Resins and Plastics**

A number of miscellaneous materials are brought together under the heading of resins and plastics. Some of these are more or less similar to factices and some are over toward the "Thiokol" type. They all make use of sulfur in some form and all appear to be polymeric.

Plastic materials are prepared by treating phenol-formaldehyde condensation products with sulfur or sulfur chloride.<sup>149b</sup> Phenols

may be condensed with formaldehyde in the presence of hydrogen sulfide<sup>26, 59a, 163</sup> or of an inorganic polysulfide.<sup>106a, 162</sup> Tar acids are condensed with sulfur at 230°.<sup>31</sup> A plastic is made from phenol, sulfur, and naphthalene.<sup>35</sup> A mixture of phenol and sulfur is heated with sodium hydroxide,<sup>61, 91, 122, 171</sup> carbonate,<sup>87, 88</sup> or nitrite,<sup>76</sup> or with a salt of a carboxylic acid.<sup>92</sup> A plastic may be made from a phenol and sulfur chloride.<sup>91, 122, 157, 184</sup>

Sulfur,<sup>93b, 106b</sup> or hydrogen sulfide,<sup>6</sup> is added during the formation of a formaldehyde-urea resin.

Resins are made from rosin and sulfur by various treatments.<sup>78, 115, 121, 178</sup> Rosin is treated with nitric acid and then fused with sodium sulfide.<sup>51</sup> An insulating varnish can be made from rosin, chinawood oil, and sodium sulfide.<sup>7</sup> Gum cumar is heated with sulfur and a filler added to make a dielectric sealing material.<sup>72</sup> Resins, natural or synthetic, can be sulfurized by adding sulfur to hot solutions of them in organic solvents.<sup>49</sup>

Resinous products are produced from divinylacetylene, sulfur, and hydrogen sulfide in the presence of an organic base.<sup>33</sup> Acetylene, hydrogen sulfide, sulfur vapor, and ammonia are passed over a metal sulfide.<sup>84</sup>

Lard oil sulfurized in a cracked paraffin is claimed as an inhibitor of oxidation.<sup>143.5</sup>

A resin is formed when rubber hydrochloride is heated with a metallic sulfide or polysulfide.<sup>188</sup>

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